

Electronic structure of the GaSe/Si(111) and InSe/Si(111) heterojunctions

M. O. D. Camara,¹ A. Mauger,¹ and I. Devos²

¹Laboratoire des Milieux Désordonnés et Hétérogènes, Case 86, 4 Place Jussieu, 75251 Paris Cedex 05, France

²Institut d'Électronique et Microélectronique du Nord, Université Lille 1, Laboratoire Central de l'EMN,

Avenue Poincaré, 59652 Villeneuve d'Ascq Cedex, France

(Received 20 November 2001; published 26 April 2002)

A tight-binding calculation of the electronic properties of the semiconductor GaSe/Si(111) and InSe/Si(111) heterojunctions is performed in a charge-dependent tight binding approach where the only Coulomb effect is a shift of all the pseudoatomic levels of a given atom at site i by the same quantity U_i . The fitting parameters U_i are determined in the framework of constrained optimization techniques using the conjugate gradient method. The band offsets at the interfaces are determined and found to be in quantitative agreement with recent experiments on both heterojunctions. In addition, this optimization technique allows us to give more insight in the charge transfer between atomic planes at the heterojunction. As a result of the strain induced by the lattice mismatch of the III-VI half layer grafted to the Si(111) surface the charge distribution does not match the simple charge neutrality condition in the case of InSe/Si(111).

DOI: 10.1103/PhysRevB.65.205308

PACS number(s): 73.20.-r, 73.61.-r

I. INTRODUCTION

Heteroepitaxy has become a key technology in fabricating electronic devices. In particular, a lot of effort has been devoted to the epitaxial growth of such layered structure materials as transition metal dichalcogenides, GaSe, or mica,¹⁻⁴ since it should accommodate large lattice mismatch. In this context, the successful attempts to grow the layered III-VI semiconductors by molecular beam epitaxy (MBE)⁵⁻⁷ has renewed the interest in these materials. Indeed, GaSe has been used as a lattice mismatch/thermal expansion buffer layer in the GaAs in the Si(111) system,⁶ of interest to the optoelectronics and photo-electronic integrated systems. These important potential applications were the motivation for extensive experimental studies of the GaSe/Si(111). Structural information on GaSe/Si(111) heterostructures have been obtained by reflection high-energy electron diffraction,^{5,7} transmission electron microscopy (TEM),⁸ and x-ray standing wave measurements.⁹ More recently, such studies have been extended to InSe/Si(111), thus completing the family of III-VI/Si(111) heterostructures obtained by MBE. In particular, the TEM revealed that the GaSe/Si(111) interface is abrupt,¹⁰ just as that of the GaSe/Si(111).⁸ Auger electron spectroscopy in GaSe/Si(111) (Refs. 5,7) and in InSe/Si(111) (Ref. 12) gave information on the surface composition. In the recent past, these analyses of structural and compositional properties have been completed by the investigation of electronic properties. The band offset at the interfaces determined from photoemission yield spectroscopy is 0.9 and 0.3–0.4 eV for GaSe/Si(111) (Ref. 11) and InSe/Si(111) (Refs. 12,13), respectively.

These numerous experimental studies contrast with the lack of theoretical work on the III-VI/Si(111) heterojunctions. In particular, the valence band offset at the interface has not been investigated theoretically yet, although this parameter in any heterojunction is crucial in determining its electronic properties, and is recognized as a key parameter in the physics of devices.¹⁴ One reason for this disparity between experiments and theory in the present case may come

from the fact that, until recently, the electronic structure of III-VI compounds has been determined in a pseudopotential approach (for a review on band calculations, see Ref. 15). Indeed, the electronic structure of a heterojunction can be obtained from first-principle calculations, based on local density formalism plus pseudopotentials.¹⁶⁻¹⁹ However, such computations are cumbersome, and in semiconductor heterojunctions a much simpler and convenient computational tool is the consistent tight-binding approach.^{20,21} Only recently did we complete a full band calculation of GaSe and InSe in the tight-binding approach.¹⁵ The purpose of this work is to extend it to the computation of the interface electronic structure between these materials and Si(111).

II. THEORY OF THE HETEROJUNCTION

GaSe and InSe belong to the same family of III-VI layered compounds and crystallize in the same symmetry. The crystallographic properties and the nature of their interface with Si(111) are then expected to be identical. This is confirmed by all the structural analyses performed so far on both GaSe/Si(111) and InSe/Si(111) interfaces. Therefore, we shall focus attention in this section on the GaSe/Si(111) interface which is the archetype of III-VI/Si(111) interfaces, and has been most studied in the literature. Then we shall see later in this work how the results can be extrapolated to InSe/Si(111).

First, the symmetry breaking at the free Si(111) surface implies the existence of dangling bonds which favor reconstructions. However, the basic two-dimensional layer of GaSe has hexagonal symmetry similar to the nonreconstructed Si(111) surface. We then expect that this symmetry is restored by the deposition of GaSe which cancels the existence of dangling bonds. Indeed, experiments have determined that the interface structure is independent of the type of initial Si(111) surface on which the epitaxial growth of thin GaSe films is achieved. To be more specific, the interface structure has been found identical for initial surfaces as different as the reconstructed 7×7 -Si(111) and the

$\sqrt{3} \times \sqrt{3}$ Ga-Si surfaces, or the H-Si(111) which is nonreconstructed since the hydrogen saturates the dangling bond.²² The only difference is that the H-terminated 1×1 surface gives the best interface quality. This interface structure can be easily understood from the nature of the chemical bonding on the III-VI compounds. One layer of GaSe is made of the piling of four atomic planes, in the sequence Se-Ga-Ga-Se. The strongest bond inside the layer is the ionocovalent Ga-Ga bond which insures the rigidity between the lower half-layer Se-Ga and the upper half layer Ga-Se. On another hand, the interaction between Se atoms on adjacent layers is weak, and is responsible for the layered nature of the compounds. Therefore, we do not expect a stable heterojunction with a Se plan as a first atomic plan above Si, since the bond involving Se is too weak. On another hand, we expect that a stable heterojunction can be formed if the upper half-layer Ga-Se is deposited on the Si surface, since the GaSe half layered is strongly bonded to Si, via the Si-Ga bond substituted to the Ga-Ga bond. Indeed, this is confirmed by the experiments which all show that the Ga atoms are covalently bonded to Si top atoms and a GaSe half-layer is grafted onto the Si(111) surface (see Ref. 22, and references therein). Yet according to the GaSe(0001) and Si(111) $3m$ symmetries, there are two different ways to build the interface if one half layer is on the the silicon substrate chosen as reference, corresponding to two orientations at 180° . The only difference between them, however, concerns the position of the Se atoms with respect to the Si atoms underneath. The interaction between these atoms, will be the order of magnitude of the interaction between a Se atom of a half-layer and the Ga atom of the other half-layer, i.e., negligible.¹⁵ Therefore, the electronic properties such as band offsets at the interface will not be sensitive to the type of orientation. As far as electronic properties are concerned, the relevant information provided by the experimental studies of the crystallographic structure is that the epitaxy between the first half-layer GaSe and Si(111) is a pseudomorphic epitaxy:²² the half-layer is laterally strained on the unrelaxed Si(111) surface, with Ga atoms on top of the Si atoms. The schematic drawing of the interface structure is reported in Fig. 1.

The structural analyses recently made by Jedrecy *et al.*^{23,24} reveal that the pilling of GaSe above the first half-layer is much more complex. The epitaxy above the first-half layer is not made plane by plane, but layer by layer, which implies the existence of steps at least one sheet high, i.e., 8 Å. Even the first layer above the half layer grafted on Si(111) is divided in domains with different orientations [referred to as A and B (Refs. 23,24)], and stacking faults are observed.⁸ Part of the domains of this first layer is relaxed with a lattice parameter close to that of bulk GaSe, but part remains laterally strained.^{23,24} Therefore, in our model to investigate electronic properties, we have restricted the GaSe (InSe) part to the half layer grafted on Si(111). Moreover, due to the large dielectric constant, the charge transfer at the heterojunction does not extend beyond the first half layer and will not be affected significantly by this restriction. It should affect quantitatively the band offsets, but still the deviation is expected to be small. Indeed, no spread out in the distribution of band offsets has ever been observed despite the distribu-

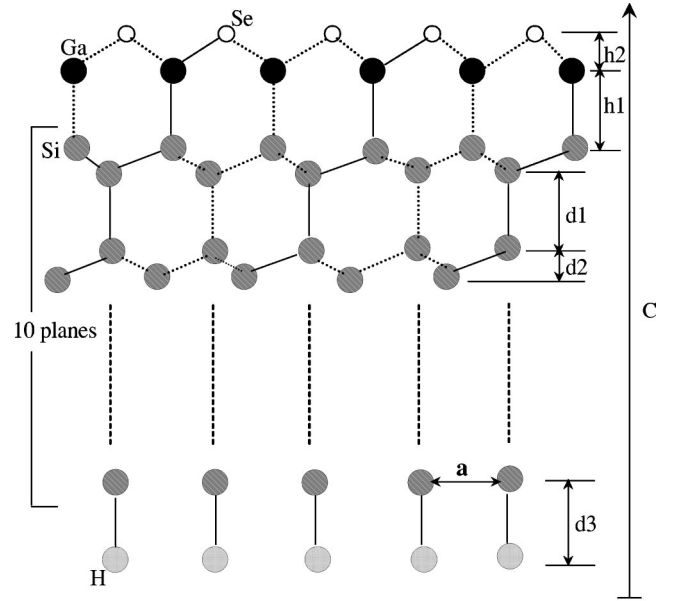


FIG. 1. Atomic structure of the (111) heterojunctions. a is the parameter of the 2D lattice in a (111) atomic plane of the Si substrate. The Si substrate is ended by a Si-H(111) surface on one hand, and by the heterojunction with the III-VI half layer on the other hand. The structure is the same for GaSe/Si(111) and InSe/Si(111). Only the numerical values of the distance h_1 between the metal (Ga,In) and the Si (111) planes at the interface, and the distance h_2 between the metal and the Se (111) atomic plane are changed (see Table I). For convenience in the tight-binding calculations, a fictive 3D lattice is generated by reproducing this structure along the c -axis perpendicular to the interface, with periodicity c also given in Table I.

tion of the GaSe layers in A and B, relaxed and strained domains. Moreover, any attempt to simulate a thicker film by a periodic arrangement of the Ga(In) and Se atoms would not match the reality either, and then would not allow a better comparison between theory and experiments. Roughly speaking, it means that in the tight-binding approach, the basis set of the Hilbert space on the GaSe side of the heterojunction will be truncated to the orbitals involving Ga and Se orbitals of the first half layer grafted on Si(111). We shall, however, indirectly take into account the fact that there is some pilling of GaSe domains above the grafted half layer by choosing the matrix elements of the tight-binding Hamiltonian equal to these which fit the dispersion relations of bulk GaSe. After these general aspects which outline the main features of our approach, let us now report how the Hamiltonian is built in practice. The first step is to determine the atomic positions which is still a structural problem, detailed hereunder in this section. The second step is to determine the matrix elements of the Hamiltonian, and is reported in the next section.

For GaSe/Si(111), the position of the atoms at the interface is known from experiments.^{8,9} The position of the atomic planes parallel to the interface is identified by their relative distance. Those are the parameters d_1, d_2, h_1, h_2 defined in Fig. 1 and reported in Table I. The position of the atoms inside the atomic planes is identified by the lattice

TABLE I. Crystallographic parameters for the GaSe/Si(111) and InSe/Si(111) heterojunctions. All the parameters are expressed in Å. The in-plane lattice parameter a , as well as the distances d_1, d_2 between (111) atomic planes are characteristics of the Si lattice, and d_3 is the Si-H bond length. Therefore, the parameters which differ in the two heterojunctions are the distance between the Si and Ga or In (111) atomic planes (h_1), the distance between the Ga or In and the Se (111) atomic plane (h_2), and the length c of the hexagonal unit cell of the pseudo-3D lattice used to build the tight-binding Hamiltonian. The data are from Refs. 8,9 for GaSe/Si(111), and determined in this work for the InSe/Si(111) heterojunction.

	GaSe/Si(111)	InSe/Si(111)
a	3.84	
d_3	1.78	
d_2	0.78	
d_1	2.35	
h_1	2.37	2.67
h_2	1.07	1.44
c	21.163	21.833

parameter of Si for the silicon part. For GaSe, the Ga atoms are located at a distance h_1 from the Si atoms at the surface, on the vertical of Si sites. We have already noticed that the symmetry allows for two orientations at 180° of the Se plane, leading to two atomic positions. A first investigation of the atomic position by the x-ray standing-wave technique favors one of them, as it locates the Se atoms on a vertical line running through the center of the triangle formed by three Ga interface atoms.^{8,9} This is thus the position we have chosen to build the heterojunction. Again the electronic properties will not be sensitive to this choice anyway, for reasons already mentioned in this section. These considerations fully determine the position of the Ga and Se atoms inside the atomic planes parallel to the interface, and the two parameters h_1 and h_2 fully determine the location of the Ga and Se atomic sites in three dimensions for the half-layer grafted on Si(111).

For InSe/Si(111), the positions of the atoms have not yet been determined experimentally. Since, however, experiments have confirmed that the structure is the same as that of GaSe/Si(111), we have extrapolated the results obtained on GaSe to the InSe half-layer grafted on Si(111), and kept the same geometry. For GaSe/Si(111), $h_1 = 2.37 \pm 0.3$ Å (Ref. 9) which, within experimental uncertainty, is the sum of the Ga and Si covalent radii ($d_{\text{Ga}} = 1.36$ Å and $d_{\text{Si}} = 1.11$ Å, respectively). As the covalent radius of In is $d_{\text{In}} = 1.56$ Å, we can then estimate for the InSe/Si(111) heterojunction $h_1 = d_{\text{In}} + d_{\text{Si}} = 2.67$ Å. The Ga-Se bond length at the interface with Si(111) is the same as in bulk GaSe.⁸ To keep constant this metal-Se bond length, the dilatation of the half-layer to adjust the lattice parameter of Si implies a decrease of h_2 with respect to bulk GaSe to $h_2 = 1.07$ Å. The same geometric argument applied to the InSe half layer grafted on Si(111) implies an increase of h_2 (as the half-layer now suffers a contraction to adjust the Si lattice parameter, up to $h_2 = 1.44$ Å. These parameters which define the atomic positions in the heterojunction are reported in Table I. The pa-

rameters a, d_1, d_2 are bulk Si parameters as the Si surface is unrelaxed, and are thus the same for both heterojunctions.

To keep the number of atoms considered finite and the dimension of the Hamiltonian matrix, it is necessary to keep the thickness of the Si layer finite. The atomic planes of Si parallel to the interface are sets of two Si-Si planes. Each set is made of two atomic planes separated by a distance d_2 , and is at a distance d_1 from the next set. In the calculations, the thickness of the layer has been chosen equal to 21.16 Å, which corresponds to five sets. We have checked that this Si layer is thick enough to simulate an infinitely thick layer, and that the electronic structure of the heterojunction remains quantitatively the same upon further increase of the number of Si layers. This Si layer is terminated by a H-Si(111) surface. This termination with hydrogen has been used to avoid the spurious localized surface states inside the energy gap due to the dangling Si bonds on the nonreconstructed bare Si(111) surface. The heterojunction on which the calculations have been made is reported in Fig. 1.

III. ELECTRONIC STRUCTURE OF HETEROJUNCTIONS

In this section, we first recall briefly how an ideal interface is described in the tight-binding scheme, and how it can be simplified by the use of the local-neutrality condition, which is a simplification successfully tested on heterojunctions involving zinc blende semiconductors in the past.

As an heterojunction is formed, there is a charge transfer through the interface, which creates a dipole. The valence band offset can thus be calculated in a model which considers either this dipole, or the related charges at the interface. Let us first consider the electric charge analysis,²⁵ which is particularly suited to the tight-binding calculations. The net electric charges Q_i carried by the atoms on site i create on site j a potential V_j which shifts the energies of the pseudo-atomic orbitals by an amount

$$V_j = \sum_i C_{ji}^{-1} Q_i \quad (1)$$

or, in matrix notation, $V = C^{-1} Q$. Whether the charges are considered as uniformly distributed in atomic planes parallel to the interface,²⁶ or localized on the atoms,²⁵ the determination of C^{-1} provides the expression of Q as a function of the potential matrix V . Starting from a set (Q_0, V_0) , we can estimate the charge transfer $Q - Q_0$ within the linear response formalism, i.e., restrict to the first order term the expansion of Q as a function of V in a Taylor series in the vicinity of (Q_0, V_0) :

$$Q - Q_0 = -\chi(V - V_0), \quad (2)$$

where χ is the susceptibility matrix. The self-consistent solution of the linear system of Eqs. (1) and (2) is

$$V = \frac{C^{-1}\chi}{I + C^{-1}\chi} V_0 + \frac{I}{I + C^{-1}\chi} C^{-1} Q_0. \quad (3)$$

Note that I in this equation is the identity matrix, and will be noted as 1 in the following. This equation only requires the

validity of the linearization in Eq. (2), i.e., that the set (V_0, Q_0) is a good approximation to the self-consistent equation. The so-called local-charge-neutrality condition, which corresponds to a charge distribution preserving the electrostatic stability of the system, i.e., preventing the system from becoming infinite far from the surface,^{27,28} is a good approximation to the self-consistent charge distribution.²⁹ Another choice is possible, such as the zero-dipole model in which the charge distribution Q_0 is such that it does not give any dipolar potential.²⁵ Both choices, however, give the same determination of the band offset, within 0.1 eV. In this work we have chosen the zero-charge (ZC) model which corresponds to the exact solution in the case when the charge is uniformly distributed in the atomic planes parallel to the interface, and set $Q_0 = Q^{ZC}$ in the equations. Equation (3) gives the potential at any distance on both sides of the interface, and then the valence band offset $\Delta E_v = \Delta(V) = V_{i=+\infty} - V_{i=-\infty}$:

$$\Delta E_v = \frac{C^{-1}\chi}{1+C^{-1}\chi} \Delta E_v^{ZC} + \frac{1}{1+C^{-1}\chi} \Delta(C^{-1}Q^{ZC}), \quad (4)$$

where $\Delta E_v^{ZC} = (V_0)_{i=+\infty} - (V_0)_{i=-\infty}$ is the valence band offset when the charge distribution is Q^{ZC} . We can have a better physical understanding of the last term of Eq. (4), if we note that the valence band offset through the heterojunction is

$$\Delta E_v = V_{\text{dip}} + \Delta E_v^0 \quad (5)$$

with V_{dip} the heterojunction dipole layer. ΔE_v^0 is so called natural band offset, defined as $\Delta E_v^0 = E_{v2} - E_{v1}$, with E_{v1}, E_{v2} the energies at the top of the valence bands referred to the electrostatic potential in the bulk infinite semiconductors 1 and 2 (Si and the III-VI compounds in the occurrence). The valence band offset in the zero charge case corresponding to the local neutral condition is [see Eq. (5)]

$$\Delta E_v^{ZC} = V_{\text{dip}}^{ZC} + \Delta E_v^0. \quad (6)$$

Since this is a good approximation to the self-consistent solution, the self-consistent result for the charge transfer δQ across the junction can be derived within the linear response theory [see Eq. (2)] which can be written

$$\delta Q = CV_{\text{dip}} = -\chi(V_{\text{dip}} - V_{\text{dip}}^{ZC}). \quad (7)$$

The solution of the linear set of Eqs. (5)–(7) gives Eq. (4), with

$$\Delta(C^{-1}Q^{ZC}) \equiv \Delta E_v^0. \quad (8)$$

The screening factor of this term in Eqs. (4),(8) defines the dielectric matrix as $\epsilon(0) = 1 + C^{-1}\chi$.

The charge transfer through the interface and the related dipole potential entering the equations correspond to a change in the Coulomb interaction. The tight-binding approach is well suited to solve this problem, since the effects of Coulomb interactions is simply to shift all the energy levels of a given atom by the same amount. Only the diagonal matrix elements of the Hamiltonian matrix are thus shifted, by an amount U_i from their value in the bulk material. In the

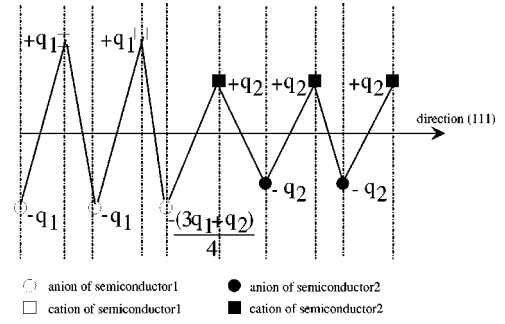


FIG. 2. Charge distribution preserving electrostatic stability in (111) heterojunctions between semiconductors, after Ref. 29 and references therein. Dashed lines represent atomic planes parallel to the interface plane.

present case, all the atoms inside a given atomic plane parallel to the interface are of the same kind and thus suffer the same potential shift. A single index i which numbers the plane position from the interface is thus sufficient to fully identify the U_i 's. The charge transfer across the interface is responsible to the dipole potential barrier, and the problem has to be solved self-consistently to determine ΔE_v . In fact, screening in such systems with high dielectric constant is very efficient, and it has been argued that a very good approximation to the fully self-consistent solution is provided by the local-charge neutrality^{29,30} in heterojunctions between semiconductors of the same class. This can be viewed from Eqs. (4),(8) as ΔE_v reduces to ΔE_v^{ZC} in the limit of large susceptibility χ , or equivalently large dielectric constant $\epsilon(0)$. This means that one can determine ΔE_v and the charge excess δq_i on atomic sites of each plane i by imposing that all the δq_i approach the local-charge neutrality condition.

Yet, there are many charge distributions which preserve the local-charge neutrality condition and electrostatic stability of the system.²⁸ As in prior works,²⁹ we consider the solution where only one plane presents a charge different from the bulk charge. This solution is displayed in Fig. 2, in the case of a (111) heterojunction with bulk charges $+q_1, -q_1$ on anion and cation of the material on one side of the interface, $+q_2, -q_2$ on the other side. The modified charge at the interface (anion plane) is $-(3q_1+q_2)/4$. In our particular case, the substrate on which the III-VI material is deposited is silicon, which is a purely covalent material, hence $q_1=0$. Since the first atom plane above Si is a Ga plane (see Fig. 1), i.e., a cation plane, the Si interface plane is the analog of an anion plane in the general case, and the formula above displayed applies, with $q_1=0$. The simplest charge distribution within the local-charge neutrality approximation is then

$$q_{i<0}^{ZC} = 0, \quad q_{i=0}^{ZC} = -q/4, \quad q_{i=1}^{ZC} = +q, \quad q_{i=2}^{ZC} = -q. \quad (9)$$

$i=0$ corresponds to the Si(111) plane at the interface. $i<0$ corresponds to the Si substrate; $i=1,2$ correspond to the metal (Ga or In) plane, and Se plane of the grafted layer, respectively.

IV. III-VI/SI(111) SYSTEMS

In this section, we first detail how the pseudo tight-binding Hamiltonian appropriate to the problem has been built. Then, we report the numerical method we have used to calculate the electrostatic charges, and the correlated band offsets³¹ along the lines of the general considerations reported in the previous section.

A. The Hamiltonian matrix

In the heterojunction model in Fig. 1, there are ten Si atomic planes, one metal and one Se atomic planes parallel to the interface, and one H-atomic plane which terminates the Si substrate, hence 13 atomic planes parallel to the interface. A fictive three-dimensional superlattice can be generated by piling series of 13 atomic planes along the c axis perpendicular to the interfaces. The unit cell of such a superlattice is hexagonal, with a basis in the plane parallel to the interface which matches that of the two-dimensional Si(111) nonreconstructed lattice, and height c which separates the 13 planes in Fig. 1. Note the unit cell contains 13 atoms (one for each atomic plane). Such a superlattice cannot exist as it would actually be unstable with respect to an infinitesimal shear force, because the basic layers of thickness c do not interact. This geometric construction must just be viewed as a mathematical convenience to restore a periodicity and invariance by translation along the c axis, so that standard tight-binding calculations of bulk materials can be used to determine the electronic structure of the heterojunction. Taking into account the 13 atoms of the unit cell and the five sp^3s^* orbitals for each atom, the tight-binding sp^3s^* pseudo-Hamiltonian matrix we are dealing with has a dimension $13 \times 5 = 65$. There is a powerful tight-binding model to deal with structural properties of covalent and ionic sp -bonded semiconductors on equal footing.³² Yet this method is not suited to the present purpose, because it is based on the use of scaling empirical laws to determine parameters such as overlap matrix elements due to nonorthogonality of the orbitals on different sites. These scaling laws are relevant to the case of these materials which crystallize in the zinc blende or the rocksalt structure. In layered compounds, however, small but significant deviations from the scaling laws arise as a result of the weaker interactions between the layers. In this particular case, the overlap matrix elements would have to be considered as fitting parameters, making the whole procedure questionable. Instead, we have recently investigated the band structure of bulk GaSe and InSe in a different tight-binding approach allowing us to get rid of the overlap elements.¹⁵ In this framework, we have determined the pseudo-Hamiltonian matrix elements in the sp^3s^* basis which reproduce the nonlocal pseudopotential band structure, as well as the optical and photoemission experimental data, the direct and indirect band gaps.¹⁵ The tight-binding parameters, i.e., diagonal and off-diagonal tight-binding Hamiltonian matrix elements for GaSe and InSe are reported in the tables of this previous work. The tight-binding parameters for Si are those reported by Vogl,³³ before the appropriate rotation is applied to the Hamiltonian to write the matrix in the appropriate hexagonal cell with lattice vectors

along the (111) directions in the interface plane, instead of the conventional (100) set. The Si-Se interactions vanish since the interactions in the pseudo-Hamiltonian are truncated to nearest neighbors (NN's) only, and NN atoms for any Se atom are Se and metal (Ga or In) atoms only. The only new matrix elements generated by the heterojunction are thus Si-metal interactions. In a tetrahedral environment, the off-diagonal parameters can be estimated from the scaling law³⁴

$$V_{\alpha\beta\gamma} = \eta_{\alpha\beta\gamma} d^{-2} \exp[-2.5(R/d - 1)], \quad (10)$$

where d is the nearest-neighbor distance between atoms of the same nature as those under consideration, R the actual distance between the atoms under consideration. The parameters $\eta_{\alpha\beta\gamma}$ have been determined by Harrison.³⁵ α, β label the orbitals s, p or s^* involved in the interaction, and γ its component σ or π . This scaling law has been used successfully to determine the electronic structure of heterojunctions between II-VI or III-V compounds in the past, including GaAs. It is then a good approximation to estimate the Ga-Si interaction. We also used this scaling law to evaluate the Si-H coupling at the bottom of the Si film in Fig. 1. Indeed, no sizable change in the density of states has been introduced by the H-Si(111) interface with this estimate of the Si-H interaction. The Se-metal interactions have been kept equal to their values determined in the bulk, since we have seen in the previous section that this bond length is the same in the bulk compound and in the heterojunction. Therefore, the tight-binding Hamiltonian matrix is built with the same tight-binding parameters as in bulk Si and GaSe or InSe defined in Sec. II and Fig. 1, plus the Si metal and Si-H interactions determined by Eq. (10) for atomic positions determined in Sec. II and Fig. 1. The pseudoatomic energies of the orbitals are shifted by the quantities U_i defined earlier in this section, which are the only fitting parameters in the problem.

B. Numerical procedures

These parameters U_i must be chosen so that the charges carried by the atoms are close to the charge distribution in Eq. (9). The fitting procedure we have chosen is the least-square fit procedure which amounts to find the minimum of the function

$$f(\{U_i\}) = \sum_i (q_i - q_i^{ZC})^2 \quad (11)$$

in the space of parameters $\{U_i\}$. According to our heterojunction model in Fig. 1, there are 13 atomic planes parallel to the interface in each basic layer, and then 13 parameters U_i . The boundary condition $U_{i=-13} = 0$ restricts the number of independent parameters to 12. The least-square fit procedure then amounts to the search for a minimum of the function f in the 12-dimensional space of parameters. The numerical procedure we have used for this purpose is the conjugate gradient method, as typified the Polak-Ribiere algorithm³⁶ we already used to determine the tight-binding parameters of GaSe and InSe.¹⁵

The calculation of f in Eq. (11) requires the calculation of the electrostatic charge carried by the atoms in the heterojunction. This charge is deduced from an integration of the density of occupied states. The expression of the density of states on an atom located in the plane i parallel to the interface takes the form

$$n_i(E) = \frac{1}{\Omega} \int \int \int_{\text{BZ}} \sum_{\alpha=1}^5 |\langle \Psi(\vec{k}) | \phi_{i,\alpha} \rangle|^2 \delta(E_k^i - E) d^3k, \quad (12)$$

where Ω is the volume of the Brillouin zone, on which the integral is performed. $\Psi(\vec{k})$ is the eigenfunction of the 65×65 Hamiltonian matrix defined earlier, for the eigenenergy $E(\vec{k})$. $\phi_{i,\alpha}$ is the pseudoatomic wave function of the orbital α for an atom in the atomic plane i , and then belongs to the set of $65 sp^3s^*$ basis functions in which the Hamiltonian matrix has been constructed. Such integrals over the Brillouin zone, can be determined by replacing the integral by a discrete summation over the “special \vec{k} points,”^{37,38} provided the Dirac functions are smoothed. For this purpose, the Dirac distribution has been replaced by a Gaussian of width $\sigma = 0.2$ eV. This value of σ is large enough to insure that the integrand is smooth so that the special point approximation is valid, and small enough so that the peaks in the density of states are not smeared out in the process. We used a set of eight special \vec{k} points in the hexagonal Brillouin zone generated by the procedure of Chadi and Cohen.³⁸ The validity of this procedure has been checked earlier, since the same set in the hexagonal Brillouin zone of bulk GaSe and InSe, and the same value of σ have been shown to reproduce quantitatively the density of states of these compounds.¹⁵ The charge carried by the atom under consideration is then given by

$$q_i = \int_{-\infty}^{E_v^i} n_i(E) dE. \quad (13)$$

E_v^i is the energy at the top of the valence band, which also depends on i , due to the offset. The procedure is thus the following. For a given choice of the set of parameters $\{U_i\}$, corresponding to one step of the minimization of f by the conjugate gradient method, the solution of the eigenproblem of the pseudo-Hamiltonian is solved, then $n_i(E)$ is determined as described above, from which E_v^i is inferred as the energy at the top of the occupied states below the energy gap, then q_i is calculated by integration of $n_i(E)$ according to Eq. (13).

The accuracy in the calculation of the band offset in our model is determined by the accuracy with which the charges are calculated. The highest accuracy is obtained by Green’s techniques by decimation techniques.^{39,40} The procedure we have used is less accurate, and to check its validity, we have used it to determine the charge on Ga and Se atoms in bulk GaSe. We find a charge $q_{\text{Ga}} = +0.66e$ and $-0.65e$ with e the absolute value of the electric charge carried by an electron, while neutrality condition that both charges are equal and opposite. A measure of the error in the determination of the charge is then $|(q_{\text{Ga}} + q_{\text{Se}})/2| = 0.005e$. It has been shown

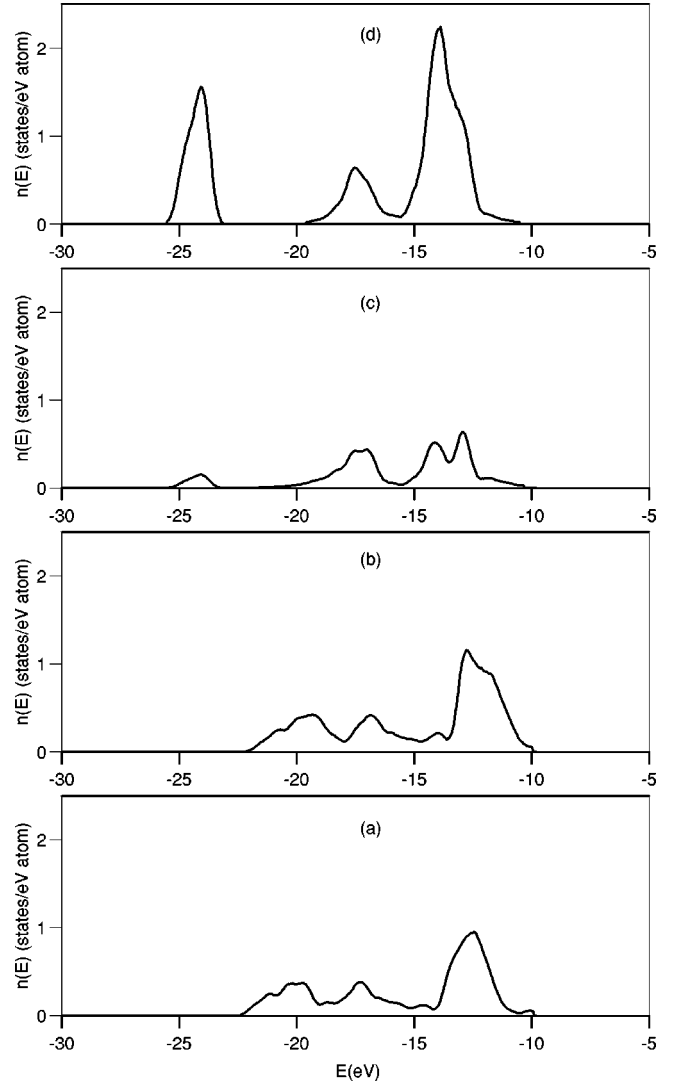


FIG. 3. Density of occupied states on a Si atom far from the interface (a) and at the interface (b), on a Ga (c), and a Se (d) atom of the half layer grafted on Si in the GaSe/Si(111) heterojunction. The origin of energies is taken in the vacuum.

that a precision of 0.001 eV in the charge results in a precision of 0.01 eV in the band offset²⁹ in CdTe/HgTe heterojunctions. The extrapolation to our case then leads to an estimate of the precision on the offset the order of 0.1 eV in our calculations.

V. THE RESULTS

In practice the boundary condition $q_{i<0} = 0$ and $U_{i=-13} = 0$ implies that $U_{i<0} \approx 0$. Therefore, the set of 12 parameters U_i is in practice reduced to four finite parameters only, which insures the unicity of the solution. The density of valence states in the different atomic planes is reported in Figs. 3 and 4 for GaSe and InSe, respectively. Note the main peaks in the density of states of Ga(In) and Se reproduce qualitatively those observed in the corresponding partial densities

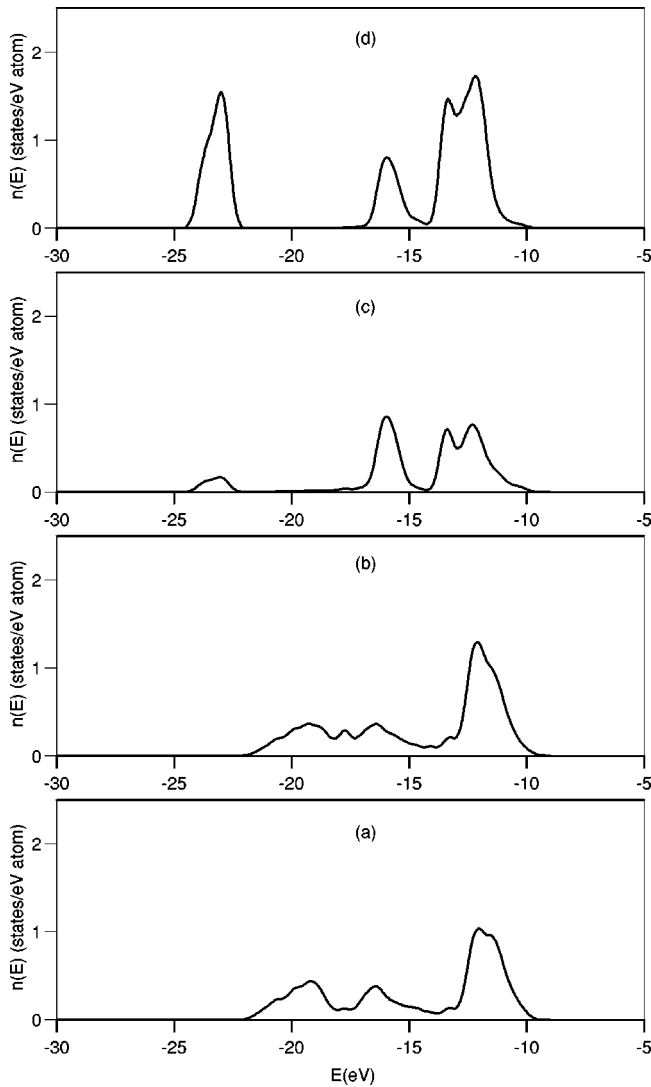


FIG. 4. Density of occupied states on a Si atom far from the interface (a) and at the interface (b), on a In (c), and a Se (d) atom of the half layer grafted on Si in the InSe/Si(111) heterojunction. The origin of energies is taken in the vacuum.

of states of bulk III-VI compounds,¹⁵ except that they are shifted in energy. The valence band offsets are reported in Table II. Our result for the interface GaSe/Si is found in agreement with most recent experimental data:¹¹ $\Delta E_v = 0.9 \pm 0.1$ eV. The difference with a smaller value (0.7 eV) published earlier has been attributed to a bad estimate of the ionization energy for the (100) face of GaSe,⁴¹ so it will not be taken into consideration. A similar quantitative agreement is found between our model and the experimental results¹³ for the offset at the InSe/Si interface.

In GaSe, a sizeable deviation with respect to the neutral charge condition is found, as the the function f takes its minimum value at $f \sim 10^{-2}$, while the charge distribution on the Si atomic plane at the interface, on the Ga atoms and on the Se atoms are, respectively, $-0.16e$, $+0.72e$, $-0.55e$. The charge transfer on the Si atom is in agreement with the pre-

TABLE II. Valence band offsets for the two heterojunctions investigated. The theoretical results are from this work, the precision is dictated by the precision with which the electrostatic charges are calculated. Experimental results are from Ref. 11 for GaSe/Si(111) and Refs. 12,13 for InSe/Si(111).

	Theory (eV)	Experiments (eV)
GaSe/Si(111)	0.98 ± 0.1	0.90 ± 0.1
InSe/Si(111)	0.32 ± 0.1	0.35 ± 0.1

dictions of Eq. (9). It is also in agreement with the analysis of core level spectra which give evidence of a charge transfer from Ga-Se to the Si layer,⁴² an additional charge transfer of about $0.08e$ between Ga and Se with respect to the bulk situation. It should be noticed that such a transfer has been inferred from optical measurements of GaSe under pressure.⁴³ Indeed, we have already noticed in Sec. II, that the distance between Ga and Se atomic planes for the half layer grafted on Si is smaller than in the bulk (see Table I). We can then expect that this charge transfer between Ga and Se in the heterojunction is due to the shrinking of the distance between the Ga and Se atomic planes equivalent to an uniaxial pressure applied along the c axis perpendicular to the interface. In InSe/Si(111), the deviation with respect to neutral charge condition is negligible, since the minimum of the function f is $f \approx 10^{-3}$ in this case. Indeed, we have noticed that the strain and the Si substrate amounts to an uniaxial dilatation instead of a pressure along the c axis.

VI. CONCLUSION

The electronic structure of GaSe/Si(111) and InSe/Si(111) has been investigated theoretically in the tight-binding approach. The band offsets are found in agreement with experiments. The use of constrained optimization techniques using the conjugate gradient method includes the constrain that the charge distribution should not depart too much from a charge neutrality condition, but at the same time it allows for a small departure from this charge neutrality condition, to adjust the fact that this condition is not exact, in particular in GaSe/Si(111), where the lattice mismatch between the two components has significant effects on the charge transfer. This result is consistent with experimental results, if we consider the effect of the constrain as effective pressure effects. The tight-binding approach combined with the constrained optimization techniques is thus a powerful tool to investigate the electronic structure of complex heterojunctions such as IV-VI/Si(111), where the interfaces are complex (no common anion, strong lattice mismatch).

ACKNOWLEDGMENTS

M.O.D.C. acknowledges financial support by Ministère de l'Éducation Nationale of Mauritania.

- ¹A. Koma, K. Sunouchi, and T. Miyajima, *J. Am. Vac. Soc. B* **3**, 724 (1985).
- ²A. Koma and K. Yoshimura, *Surf. Sci.* **174**, 556 (1986).
- ³K. Ueno, T. Shimada, K. Saiki, and A. Koma, *Appl. Phys. Lett.* **56**, 327 (1990).
- ⁴K. Ueno, H. Abe, K. Sakai, A. Koma, H. Oigawa, and Y. Nannichi, *Surf. Sci.* **267**, 43 (1992).
- ⁵K. Y. Liu, K. Ueno, Y. Fujikawa, K. Saiki, and A. Koma, *Jpn. J. Appl. Phys., Part 2* **32**, L434 (1993).
- ⁶J. E. Palmer, T. Saitoh, T. Yodo, and M. Tamura, *Jpn. J. Appl. Phys., Part 2* **32**, L1126 (1993).
- ⁷V. Le Thanh, M. Eddrief, C. Sébenne, A. Sacuto, and M. Balkanski, *J. Cryst. Growth* **135**, 1 (1994).
- ⁸A. Koëbel, Y. Zheng, J. F. Pétroff, M. Eddrief, V. Le Thanh, and C. Sébenne, *J. Cryst. Growth* **154**, 269 (1995).
- ⁹Y. Zheng, A. Koëbel, J. F. Pétroff, J. C. Bouillard, B. Capelle, and M. Eddrief, *J. Cryst. Growth* **162**, 135 (1996).
- ¹⁰A. Koëbel, Ph.D. thesis, Université Paris VII, 1997.
- ¹¹H. Reqqass, J. P. Lacharme, M. Eddrief, C. A. Sébenne, Le Thanh Vinh, Y. Zheng, and J. F. Pétroff, *Appl. Surf. Sci.* **104-105**, 557 (1996).
- ¹²S. El Monkad, M. Eddrief, J. P. Lacharme, K. Amimer, and C. A. Sébenne, *Surf. Sci.* **352-354**, 833 (1996).
- ¹³S. El Monkad, Ph.D. thesis, Université Paris-Sud, Orsay 1997.
- ¹⁴F. Capasso, *Surf. Sci.* **142**, 513 (1984), and references therein.
- ¹⁵M. O. D. Camara, A. Mauger, and I. Devos, *Phys. Rev. B* **65**, 125206 (2002).
- ¹⁶G. A. Baraff, J. A. Appelbaum, and D. R. Hamann, *Phys. Rev. Lett.* **38**, 237 (1977).
- ¹⁷W. E. Pickett, S. G. Louie, and M. L. Cohen, *Phys. Rev. B* **17**, 815 (1978).
- ¹⁸K. Kunc and R. M. Martin, *Phys. Rev. B* **24**, 3445 (1981).
- ¹⁹C. G. Van de Walle and R. M. Martin, *J. Vac. Sci. Technol. B* **4**, 1055 (1986).
- ²⁰C. Priester, G. Allan, and M. Lannoo, *Phys. Rev. B* **33**, 7386 (1986).
- ²¹G. Platero, J. Sanchez-Dehesa, C. Tejedor, and F. Flores, *Surf. Sci.* **168**, 553 (1986).
- ²²A. Koëbel, Y. Zheng, J. F. Pétroff, J. C. Bouillard, J. C. Capelle, and M. Eddrief, *Phys. Rev. B* **56**, 12 296 (1997).
- ²³N. Jedrecy, R. Pinchaux, and M. Eddrief, *Phys. Rev. B* **56**, 9583 (1995).
- ²⁴N. Jedrecy, R. Pinchaux, and M. Eddrief, *Physica B* **248**, 67 (1998).
- ²⁵C. Priester, G. Allan, and M. Lannoo, *J. Vac. Sci. Technol. B* **6**, 1290 (1988).
- ²⁶A. Muñoz, J. C. Duran, and F. Flores, *Phys. Rev. B* **35**, 7721 (1987).
- ²⁷R. W. Nosker, P. Mark, and I. D. Levine, *Surf. Sci.* **19**, 291 (1970).
- ²⁸P. Masri and M. Lannoo, *Surf. Sci.* **52**, 377 (1975).
- ²⁹B. Haussy, C. Priester, G. Allan, and M. Lannoo, *Phys. Rev. B* **36**, 1105 (1987).
- ³⁰W. A. Harrison and J. Tersoff, *J. Vac. Sci. Technol. B* **4**, 1068 (1986).
- ³¹M. O. D. Camara, Ph.D. thesis, Université Paris 6, 2000.
- ³²J. A. Majewski and P. Vogl, *Phys. Rev. B* **35**, 9666 (1987).
- ³³P. Vogl, H. P. Hajalmarson, and J. D. Dow, *J. Phys. Chem. Solids* **44**, 365 (1983).
- ³⁴J. O. Fourcade, A. Ibanez, J. C. Jumas, M. Maurin, I. Lefèbre, P. Lippens, M. Lannoo, and G. Allan, *J. Solid State Chem.* **87**, 366 (1990).
- ³⁵W. A. Harrison, *Phys. Rev. B* **24**, 5835 (1981).
- ³⁶See, for example, W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran, The Art of Scientific Computing* (Cambridge University Press, Cambridge, 1992), p. 387.
- ³⁷A. Baldereschi, *Phys. Rev. B* **7**, 5212 (1973).
- ³⁸D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **7**, 692 (1973).
- ³⁹F. Guinea, J. Sanchez-Dehesa, and F. Flores, *J. Phys. C* **16**, 6499 (1983).
- ⁴⁰F. Guinea, C. Tejedor, F. Flores, and E. Louis, *Phys. Rev. B* **28**, 4397 (1983).
- ⁴¹H. Reqqass, J. P. Lacharme, C. A. Sébenne, M. Eddrief, and Le Thanh Vinh, *Appl. Surf. Sci.* **92**, 357 (1996).
- ⁴²A. Amokrane, C. A. Sébenne, A. Cricenti, C. Ottaviani, F. Proix, and M. Eddrief, *Appl. Surf. Sci.* **123-124**, 619 (1998).
- ⁴³M. Gauthier, A. Polian, J. M. Besson, and A. Chevy, *Phys. Rev. B* **40**, 3837 (1989).