Theoretical studies of electronic and structural properties of the Si/GaP(110) interface

Che Jingguang
Physics Department, Fudan University, Shanghai 200433, People's Republic of China

Zhang Kaiming and Xie Xide
China Center of Advanced Science and Technology (World Laboratory), P.O. Box 8730, Beijing, People's Republic of China and Physics Department, Fudan University, Shanghai 200433, People's Republic of China

(Received 9 June 1994)

The electronic and structural properties of the Si/GaP(110) interface with various thicknesses of Si overlayers on a GaP(110) semi-infinite substrate have been studied by using the self-consistent semiempirical tight-binding method with the charge neutrality condition. In addition, we present an approach to calculating the variation of band offsets with the number of adlayers during the Si/GaP(110) interface formation. In the calculation, the influence of surface and interface dipoles are taken into account. The calculation shows that the band offset exists with the first Si adlayer on the GaP(110) substrate and increases continuously with the number of Si overlayers. When reaching five or six Si layers, the band offset is close to the final value, 0.43 eV, of the Si/GaP(110) interface of two semi-infinite crystals.

I. INTRODUCTION

In recent years, the electronic properties of heterostructures have attracted the attention of both experimental and theoretical studies due to the great technological importance of such systems.[1,2] The band offset at an interface is a key parameter in determining the electrical and optical properties of heterostructures. Some theoretical methods have been suggested and have successfully predicted band offsets of many heterostructures; the results are in quite good agreement with the experimental data. However, some exceptions exist, one of which is the Si/GaP(110) interface. The value of band offset determined by the synchrotron-radiation photoemission by Perfetti *et al.*[3] is 0.66 eV, and further corrected to 0.80 eV by the more exact examination of the Fermi level.[4] Katnani and Margaritando[5] gave a value of 0.95 eV. The reported values by theoretical calculations based on linear muffin-tin orbitals or *ab initio* pseudopotential with the supercell model ranged between 0.27 and 0.61 eV.[6,7]

The present study is motivated by the discrepancies between the experimental and theoretical results, as well as between results obtained by various theoretical groups. An interface may be experimentally formed by an overlayer on an original substrate surface. Detailed studies of the microscopic properties during the formation of an interface can give a better understanding of the electrical and optical properties of heterostructures. Therefore, we will investigate the electronic and structural properties of the Si/GaP(110) interface with various thicknesses of Si overlayers on a semi-infinite GaP(110) substrate and calculate the variations of the band offset on an atomic scale during the Si/GaP(110) interface formation.

II. METHODS

The self-consistent semiempirical tight-binding method (SC-SETBM) combined with a local charge neutrality condition introduced by Muñoz, Sánchez, and Flores,[13] is used. This method, which has successfully predicted band offsets of many heterostructures, is based on the fact that an inappropriate offset of two band structures at the interface can induce a charge transfer across the interface and the interface dipole thus formed will, in turn, screen more charge transfer. The method is described and discussed in detail in Ref. 13. If Δn_L represents the net charge on the Lth atomic layer and $d_{L,L-1}$ the distance between the Lth and $(L-1)$th layer, an electrostatic potential V_L on the Lth layer induced by the charge transfer can be given by

$$V_L = V_{L-1} + \frac{4\pi d_{L,L-1}}{S} \sum_{j=L_{\min}}^{L-1} \Delta n_j \ , \tag{1}$$

where S is the area per atom in the two-dimensional unit cell. V_L is a perturbation potential that shifts the sp^3 level of atoms in the Lth layer. Since $4\pi d_{L,L-1}/S$ is about 30 eV and the perturbation can only affect two or three layers, moreover, the charge transfer only covers a finite number of layers, the following conditions

$$\sum_{L=L_{\min}}^{L_{\max}} \Delta n_L = 0 \tag{2}$$

and

$$\Delta n_L = 0 \quad (\text{for } L > L_{\max} \text{ and } L < L_{\min}) \tag{3}$$

can be used. This local charge neutrality condition defines the self-consistent condition and allows us to calculate by successive iteration the final perturbation potential V_L, which will be used to determine the band offset across the interface of material A and B, i.e., from Eqs. (1), (2), and (3) we have

$$V_L(A) \equiv V_{L_{\max}}(A) \quad (\text{for } L > L_{\max}) \tag{4}$$

and

$$V_L(B) \equiv V_{L_{\min}}(B) \quad (\text{for } L < L_{\min}) . \tag{5}$$

For an interface with two semi-infinite crystals, the band offset can be simply determined by Eqs. (4) and (5). The shift of sp^3 level will directly give the shift of the valence-band maximum (VBM) for an infinite (or a semi-infinite) crystal in the framework of ETBM. The band offset of the interface is given by

$$\Delta E_V(A/B) = V_{L_{\max}}(A) - V_{L_{\min}}(B) . \tag{6}$$

If the charge transfer induced by the interface is assumed to be able to penetrate only three layers on each side of the interface and the interface of two materials A and B is located between $L=1$ and $L=-1$ ($L=0$ is omitted), then $L_{\max}$ in Eq. (6) is equal to L_3 and $L_{\min}$ takes the value of L_{-3}.

However, for an interface with an overlayer (A) on a semi-infinite substrate (B), the above procedure cannot be used. Both the band discontinuity and the surface itself will induce a charge transfer. For a finite overlayer, Eq. (4) can no longer be valid. In addition, the shift of the VBM of an overlayer does not follow the shift of an sp^3 level. In other words, the existence of the surface makes it difficult to calculate the band offset of a system with an overlayer on a semi-infinite substrate using the SC-SETBM.

In the following, a real example of self-consistent layer potentials will be given for a system with 11 layers on a semi-infinite substrate as shown in Fig. 1. The influence of the surface on calculating the band offset of an overlayer system will be considered with the help of this figure. The surface layer is labeled $L=11$, the interface is between the label $L=1$ and $L=-1$ ($L=0$ is omitted). Only three substrate layers are sketched in this figure. From Fig. 1, it can be seen that the layer potentials in $L=3\sim-3$ are induced mainly by the band discontinuity at the interface and that in $L=11\sim8$ mainly by the surface. Therefore, a system with a thick overlayer can be divided into three regions, i.e., the surface region, which consists of the top four layers, the interface region consisting of three layers on each side of the interface, and the transition region. In order to remove the surface influence on calculating the band offset, the layer potential in the last layer of the transition region will be treated as a constant extending to the surface region and layer potentials thus obtained are defined as extracted potentials. But for a system with a thin overlayer, the transition region no longer exists and the charge transfers induced both by the surface and by the band discontinuity are mixed. Therefore, for a thin overlayer system, we have to subtract the corresponding clean surface potential from that of the system with a thin overlayer to generate the extracted potentials. Such extracted potentials in an overlayer are approximately induced only by the band discontinuity across the interface and can be used to calculate the band offset of a thin overlayer system. Since the shift of the VBM of an overlayer does not follow the shift of the sp^3 level, the VBM will be determined with the help of calculating the local densities of states (LDOS) at the Γ-point, i.e., the zero of the linear extrapolation of the LDOS's edge at the Γ point. Thus, the band offset of a system with an overlayer on a semi-infinite substrate is given by

$$\Delta E_V(A/B) = E_{\mathrm{VBM}}(V_{\mathrm{ext}}) - V_{-3}(B) , \tag{7}$$

where $E_{\mathrm{VBM}}(V_{\mathrm{ext}})$ is the valence-band maximum with the extracted potentials as above defined for a thick or a thin overlayer.

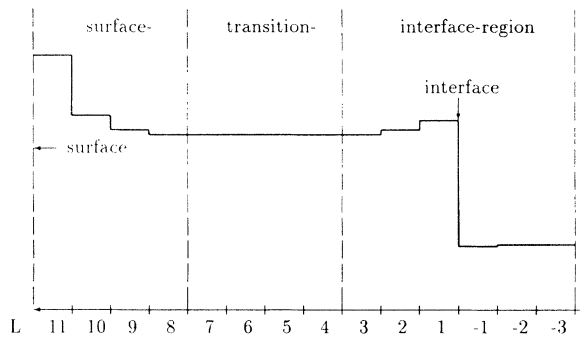

FIG. 1. Schematic description of the change of layer potential at the center of each layer in the surface, interface, and transition region for a system with 11 overlayers on a semi-infinite substrate (only three substrate layers are included) in the 110 orientation.

Due to the complexity of the system considered, we restrict our calculation to the empirical tight-binding method. The electronic properties of bulk GaP and Si are described by means of empirical tight-binding parameters considered up to the second-nearest neighbors. These parameters were obtained by fitting bulk band structures to the corresponding experimental data by Kalla and Pollmann[9] for GaP and by Pandey and Phillips[8] for Si, respectively. The interaction parameters between Si and GaP were determined by taking chemical trends into account as discussed in Ref. 9. The justification of using this method is described in detail in Ref. 10. It is worth mentioning that in the framework of ETBM, the band offset is strongly dominated by the energy differences of the sp^3 levels between the two materials rather than by the fine details of their mutual interactions across the interface. The lack of periodicity perpendicular to the surface (interface) and the relaxation of the surface are described with the scattering theoretical method,[11] the so-called resolvent Green's function method. The net charge in the Lth atomic layer, Δn_L, in Eq. (1) will be calculated by the Green's function.

The lattice mismatch between GaP and Si is about 0.36%, which can be neglected. It was shown experimentally that no dislocations of the Si/GaP interface exist when the layer thickness is less than 90 nm.[12] Therefore, an ideal, abrupt interface geometry will be used throughout the calculation in the present work. The relaxation of the surface of a system with an overlayer on a semi-infinite substrate will be taken into account and will be determined by calculating Hellmann-Feynman forces. A side view of the relaxed (110) surface of a zinc-blende crystal is shown in Fig. 2.

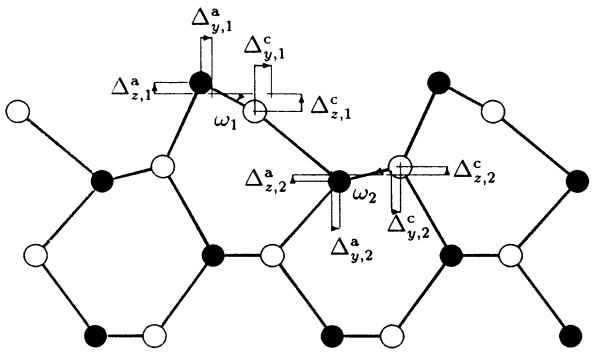

FIG. 2. Side view of the relaxation geometry for a 110 surface of the zinc-blende structure (●, anion; ○, cation). Δ^c_z, Δ^c_y, Δ^a_z, and Δ^a_y represent the shift from ideal position perpendicular, as well as parallel, to the surface, respectively. The index c stands for cations and a for anions. ω indicates the angle of relaxation.

III. RESULTS AND DISCUSSIONS

Using the above-mentioned methods, we have calculated electronic and structural properties of the Si/GaP (110) interface with various thicknesses of Si overlayers on a GaP(110) semi-infinite substrate. The results are obtained in such a way that both procedures, optimizing the relaxed structure of free surface and calculating layer potential, are alternatively performed until the self-consistency is achieved, i.e., the Hellmann-Feynman forces on all relaxed atoms are smaller than 10^{-5} eV/Å and the self-consistent accuracy of layer potentials is better than 0.005 eV.

We have considered the relaxation of the subsurface layer for the Si(110) and GaP(110) surface, but the results show that it is very small. The relaxation structure parameters of the Si(110) subsurface layer are $\Delta^c_{z,2}=0.01$ Å, $\Delta^c_{y,2}=0.00$ Å, $\Delta^a_{z,2}=-0.02$ Å, $\Delta^a_{y,2}=0.02$ Å, and $\omega_2=-0.9°$, whereas that of the upmost surface layer are $\Delta^c_{z,1}=-0.38$ Å, $\Delta^c_{y,1}=-0.33$ Å, $\Delta^a_{z,1}=0.16$ Å, $\Delta^a_{y,1}=-0.19$ Å, and $\omega_1=23.8°$ [(see Fig. 2) the notations, Δ^c for cation and Δ^a for anion, as defined in Fig. 2, are the same for the Si(110) surface]. For the GaP(110) surface, the parameters are $\Delta^c_{z,2}=0.03$ Å, $\Delta^c_{y,2}=0.01$ Å, $\Delta^a_{z,2}=-0.02$ Å, $\Delta^a_{y,2}=0.02$ Å, and $\omega_2=-1.9°$ against $\Delta^c_{z,1}=-0.41$ Å, $\Delta^c_{y,1}=-0.36$ Å, $\Delta^a_{z,1}=0.21$ Å, $\Delta^a_{y,1}=-0.22$ Å, and $\omega_1=27.1°$. Therefore, only the relaxation of the upmost surface layer is taken into account throughout our calculations.

The calculated optimal structure of free surfaces of overlayer systems are given in Table I, where we use Si_1-GaP, Si_2-GaP, Si_3-GaP, . . . , to represent the system of 1,2,3, . . . , Si layers on a semi-infinite GaP(110) substrate. For comparison, the results of the relaxed clean Si(110) semi-infinite surface are also given in Table I. The Si adlayers can be seen as the extension of the GaP structure in Fig. 2, thus, the notation Δ^c for a Si atom means that the Si atom occupies a position of a cation in the zinc-blende structure and so does Δ^a for a position of an anion. The calculation of the Si(110) surface is the same as mentioned above, i.e., optimizing the relaxed surface geometry and calculating layer potential until the self-consistency is achieved. For the Si(110) surface, we get two energetically equivalent geometries due to the symmetry of both Si atoms in the unit cell. It is shown that the optimal geometries of more than three or four Si layers on GaP(110) are very close to that of the clean Si(110) surface. This means that if there are more than three Si layers on the GaP substrate, the influence of the interface on the surface geometry is very small, whereas it will be seen that there is still an influence on the surface potential up to seven Si adlayers due to the charge transfer.

The self-consistent data of layer potentials for different thickness of Si overlayers on the GaP(110) substrate are listed in Table II, Si_1,Si_2,Si_3, . . . , are used to represent the system of 1,2,3,..., Si layers on a semi-infinite GaP(110) substrate. For comparison, the results of the relaxed clean Si(110) surface and of the previous work[14] for the two semi-infinite crystals Si/GaP(110) interface are also given in Table II, which are represented by Si and Si_∞, respectively. The layer index $-3, -2, -1$ corre-

TABLE I. The optimal geometries of free surface of an Si overlayer on GaP(110) substrate and of the clean Si(110) surface.

	Δ^c_z (Å)	Δ^c_y (Å)	Δ^a_z (Å)	Δ^a_y (Å)	ω (deg)
Si_1-GaP	0.22	0.26	−0.38	0.41	−26.1
Si_2-GaP	−0.32	−0.31	0.16	−0.19	21.4
Si_3-GaP	0.17	0.21	−0.37	0.34	−23.5
Si_4-GaP	−0.37	−0.34	0.17	−0.21	23.4
Si_5-GaP	0.17	0.21	−0.36	0.34	−23.4
Si_6-GaP	−0.36	−0.34	0.17	−0.21	23.4
Si_7-GaP	0.17	0.21	−0.36	0.34	−23.4
Si_8-GaP	−0.36	−0.34	0.17	−0.21	23.4
Si_9-GaP	0.17	0.21	−0.36	0.34	−23.4
Si_{10}-GaP	−0.36	−0.34	0.17	−0.21	23.4
Si_{11}-GaP	0.17	0.21	−0.36	0.34	−23.4
Si_{12}-GaP	−0.36	−0.34	0.17	−0.21	23.4
	0.17	0.21	−0.36	0.34	−23.4
Si(110)					
	−0.36	−0.34	0.17	−0.21	23.4

TABLE II. Layer potentials of Si-GaP(110) systems in eV. -3, -2, and -1 correspond to layers of the GaP(110) substrate and 1,2,...,12 to adlayers of Si. Si_1, Si_2,Si_3, ..., Si_∞ denote systems of different thickness of Si layers on the GaP(110) substrate (refer to Fig. 1) and Si denotes the relaxed Si(110) surface.

	Si	Si_1	Si_2	Si_3	Si_4	Si_5	Si_6	Si_7	Si_8	Si_9	Si_{10}	Si_{11}	Si_{12}	Si_∞
		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	-3	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GaP	-2	0.11	-0.01	-0.02	-0.02	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03
	-1	1.19	0.61	0.54	0.50	0.48	0.49	0.49	0.48	0.48	0.48	0.48	0.48	0.48
	1	0.00	1.17	0.64	0.50	0.45	0.45	0.44	0.44	0.44	0.44	0.44	0.44	0.44
	2	0.00		1.18	0.63	0.49	0.45	0.44	0.44	0.43	0.43	0.43	0.43	0.43
	3	0.00			1.18	0.63	0.50	0.44	0.44	0.43	0.43	0.43	0.43	
	4	0.00				1.19	0.64	0.48	0.44	0.43	0.43	0.43	0.43	
	5	0.00					1.19	0.62	0.48	0.43	0.43	0.43	0.43	
	6	0.00						1.16	0.61	0.48	0.43	0.43	0.43	
Si	7	0.00							1.15	0.61	0.47	0.43	0.43	
	8	0.00								1.15	0.61	0.47	0.43	
	9	0.00									1.15	0.61	0.47	
	10	0.02										1.15	0.61	
	11	0.18											1.15	
	12	0.73												1.15

sponds to GaP layers and 1,2,3,..., to Si layers (Fig. 1).

Variations of layer potentials with number of Si adlayers on the semi-infinite GaP(110) substrate are shown in Table II. The layer potentials of the GaP(110) substrate, namely the data in $L=-1,-2,-3$, remain almost unchanged with various thicknesses of Si layers, except the Si_1-GaP system since the $L=-1$ layer of Si_1-GaP is at the same time also the subsurface layer. For more than six Si layers on the GaP(110) substrate, the Si layer potentials in the $L=1,2,3$ layer do not depend on the number of Si layers and are almost identical since they are dominated mainly by the band discontinuity at the interface. The difference of layer potentials in the three top Si surface layers is smaller than 0.04 eV as one goes from 1 adlayer to 12 layers. The stable values of these three layer potentials for 10 to 12 adlayers on the GaP(110) substrate are 1.15, 0.61, and 0.47 eV. If one subtracts the corresponding layer potentials of the clean relaxed Si(110) surface, 0.73, 0.18, and 0.02 eV given in the first column of Table II, from the values in these three layers, one has 0.42, 0.43, and 0.45 eV. They agree quite well with the layer potential in the transition region, 0.43 eV. This fact supports our treatment for a thin overlayer system in generating the extracted potentials. A system with seven Si layers on the GaP(110) is a system without a transition region according to our definition. However, the layer potentials of this system in the $L=2,3,4$ layer take the same value, 0.44 eV. It means that being two layers away from both the interface and the surface the charge transfers are very small, thus, for a system with seven Si layers, these three layers can be considered as the transition region. For systems with more than seven Si layers, the small change of the layer potentials in the surface region (in the upmost three layers) as well as in the interface region (in the $L=1,2,3$ layer) shows that the interaction between the surface and the interface quickly diminishes with the increase of the number of Si layers. Therefore, the layer potentials in the transition region remain almost unchanged and are, in fact, the extension of the potential in the last layer of the interface region. In light of these variations of layer potentials, one can conclude that the division of an overlayer system into three regions can be justified and the method of using the extracted potentials to determine the band offset is also reasonable.

With the help of the LDOS at the Γ point, we determine band offsets of the systems with 1 to 12 Si layers on a semi-infinite GaP(110) crystal. The results are given in Table III. Since the band offset is dominated by the electronic properties at the interface, it can be expected that the band offset during the interface formation will have a stable value when the overlayer on the substrate reaches a sufficient thickness. Our results show that the band offset exists with the first Si adlayer on the GaP(110) substrate and increases continuously with the thickness of Si overlayers. When reaching five or six Si layers, the band offset is close to the final value, 0.43 eV, which is the band offset of two semi-infinite crystals Si/GaP(110) interface.[14] Our result shows that a stable band offset is reached at five or six Si layers on the GaP(110) substrate. The results agrees very well with the experimental result

TABLE III. Change of band offset during Si/GaP(110) interface formation in eV. Si_1, Si_2, Si_3, . . . , Si_∞ represent systems of different thickness of Si layers on the GaP(110) substrate.

	Si_1	Si_2	Si_3	Si_4	Si_5	Si_6	Si_7	Si_8	Si_9	Si_{10}	Si_{11}	Si_{12}	Si_∞
ΔE_v	0.15	0.21	0.31	0.36	0.39	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43

of Perfertti *et al.*[4]

The present calculations show that for more than five Si layers on the GaP(110) substrate, the layer potential in the Si interface layer ($L=1$) is greater than that in the Si subinterface layers ($L=2$ and $L=3$). It means that there exists charge transfer both from the GaP substrate and from the Si subinterface to the Si interface. It is caused by the filling of charges in the Si subinterface layers into the interface states of Si-GaP at the Si interface layer. Such a feature is somewhat different from other similar heterostuctures, e.g., Ge-GaAs(110) heterostructure.[14] The previous theoretical calculations by other authors[6,7] were carried out using a supercell of three Si layers and three GaP layers. The details of the above charge transfer could not be included in such a supercell model. It may be one of the reasons for the discrepancies of band offset between different theoretical calculations for the Si/GaP(110) interface.

IV. CONCLUSIONS

In conclusion, we have calculated electronic and structural properties during the Si/GaP(110) interface formation. In order to estimate the band offset of an overlayer system, we have introduced an approach based on the self-consistent semiempirical tight-binding approximation and the local charge neutrality condition. The influence of the interface as well as that of surface dipoles have been taken into account. The obtained results give a good support to our approach to calculating the band offset across an interface with an overlayer on a semi-infinite substrate. The band offset is formed with one Si adlayer on the GaP(110) substrate and increases continuously with the number of Si layers. The stable value, 0.43 eV, is reached at about five Si layers on the GaP(110) substrate. We have found that the layer potentials matched at the Si/GaP(110) interface are somewhat different from that of other similar heterostructures. The band offset of this system is more complicated; this might be one of the reasons for the discrepancies of band offset between various theories for the Si/GaP(110) interface.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation of China.

[1]R. Bauer and G. Margaritondo, Phys. Today, **40** (1), 3 (1987).
[2]F. Flores and C. Tejedor, J. Phys. C **20**, 145 (1987).
[3]P. Perfetti, F. Patella, F. Sette, C. Quaresima, C. Capasso, A. Savoia, and G. Margaritondo, Phys. Rev. B **29**, 5941 (1984).
[4]P. Perfetti, F. Patella, F. Sette, C. Quaresima, C. Capasso, A. Savoia, and G. Margaritondo, Phys. Rev. B **30**, 4533 (1984).
[5]A. D. Katnani and G. Margaritondo, Phys. Rev. B **28**, 1944 (1983).
[6]N. E. Christensen, Phys. Rev. B **37**, 4528 (1988).
[7]C. G. van de Walle and R. M. Martin, Phys. Rev. B **35**, 8159 (1987).
[8]K. C. Pandey and J. C. Phillips, Phys. Rev. B **13**, 750 (1976).
[9]R. Kalla and J. Pollmann, Surf. Sci. **200**, 80 (1988).
[10]P. Krüger and J. Pollmann, Phys. Rev. B **30**, 3406 (1984).
[11]J. Pollmann and S. T. Pantelides, Phys. Rev. B **21**, 709 (1980).
[12]Tetsuo Soga, Takashi Jimbo, and Masayoshi Umeno, Appl. Phys. Lett. **61**, 2543 (1993).
[13]A. Muñoz, J. Sánchez, and F. Flores, Europhys. Lett. **2**, 385 (1986).
[14]Jingguang Che, Doctoral thesis, University of Münster, Germany, 1991.