PHYSICAL REVIEW B VOLUME 35, NUMBER 14 15 MAY 1987-I

Theoretical calculation for a ZnSe-Ge(110) heterojunction with an ultrathin intralayer

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(Received 24 December 1986)

We present a consistent tight-binding calculation of the ZnSe-Ge(110) heterojunction with an Al monolayer between the two semiconductors. Our results are in reasonable agreement with the experimental evidence found by Niles *et al.*, showing that an ideal interface is an adequate model to explain the interface behavior. The shift in the valence-band offset due to the Al intralayer is interpreted as a shift in the difference between the charge-neutrality levels of both semiconductors, induced by the deposited intralayer.

The band discontinuities in heterojunctions are one of the crucial parameters determining the behavior of superlattice devices, channeling diodes, and staircase structures.[1] The possibility of controlling the band lineup between two semiconductors is a very attractive problem of the physics of devices. In the last few years, experimental and theoretical results have produced substantial progress in understanding the nature of the band discontinuities.[2-7] One important result in this area showed that drastic changes in the interface preparation and structure failed to produce detectable changes in the valence-band discontinuity, ΔE_V, of GaAs-Ge.[8] Recently, Niles *et al.*[9,10] presented the first evidence obtained with photoemission spectroscopy that the band lineup can be changed by depositing an ultrathin intralayer between the semiconductors.

The purpose of this Brief Report is to present the first theoretical calculation of a heterojunction [ZnSe-Ge(110)] with an ultrathin intralayer of Al, this being one of the systems studied by Niles *et al.*[10] In our model (Fig. 1), we assume that the two crystals extend ideally to the interface, with a monolayer of Al between the two semiconductors. We have also assumed that the metallic intralayer forms a (110) face similar to that of the Al crystal. In this two-dimensional layer there are two kinds of atom, one is coordinated to ZnSe as the cation atom of the ideally continued crystal of the semiconductor, while the other one is located in the same way with respect to Ge [notice that the ZnSe and Ge structures match well, and that the (110) faces of both crystals also match well to the 90°-rotated (110) Al face]. Although there is no experimental evidence supporting this model, it is well known that Al forms abrupt interfaces with many semiconductors.[11] Moreover, for a few known cases [say,[12] Al on GaAs(100)], the adatoms seem to form a metal layer of the actual metal structure matching the semiconductor surface: this is the basic assumption guiding us in defining the geometrical model at the interface.

We have obtained the electronic properties of that interface by using a tight-binding model that incorporates the concept of the charge-neutrality level.[13-15] For an ideal heterojunction (with no intralayer), this model has been successfully used to predict the semiconductor band discontinuities.[4,15] In a simpler approximation,[7] charge neutrality levels have been calculated for each semiconductor forming the junction, and band offsets have been obtained by aligning the neutrality levels of both crystals. In the tight-binding model used here, charge neutrality conditions are explicitly included in the consistency of the problem.

The electronic band structures of ZnSe and Ge are described by means of sp^3s^* hybrid orbitals in each atom, and interactions that extend up to first neighbors are included.[16] For an ideal heterojunction (with no intralayer), the interactions between ZnSe and Ge have been obtained

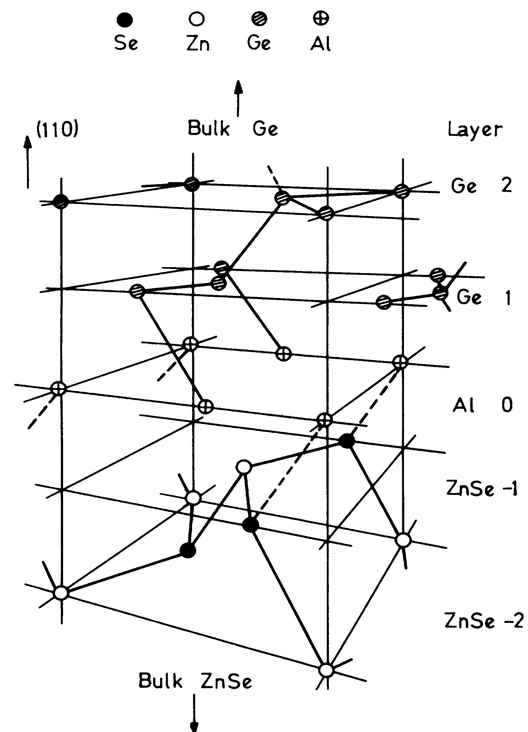

FIG. 1. Geometry of the model considered for the ZnSe-Al-Ge(110) heterojunction.

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by taking an average between those of each crystal. For the intralayer, we also used sp^3s^* hybrid orbitals with the corresponding interactions defined in the following way: (i) the Al-Ge interactions are obtained by taking an average of interactions[16] for AlAs and Ge (AlAs is taken as representative of the different III-V semiconductors having Al as a cation); (ii) the Al-Zn and Al-Se cases are obtained by averaging the AlAs and the ZnSe interactions; and (iii) finally, the Al-Al interactions have been calculated by using Harrison's prescription[17] with an inverse square law for the dependence on the Al-Al distance (see Table I).

On the other hand, in the initial Hamiltonian we define the mean level of each crystal and the intralayer in the following way: for ZnSe and Ge the mean level is adjusted to give the experimental electron affinity, χ, of each semiconductor ($\chi_{\text{ZnSe}}=4.09$ eV and $\chi_{\text{Ge}}=4.13$ eV).[18] For the intralayer, the orbital mean level is adjusted to give the metal work function of Al ($\phi_{\text{Al}(110)}=4.06$ eV) when the monolayer is assumed to be decoupled from the two semiconductors. These initial mean levels are modified by the diagonal perturbations we introduce at each layer of the interface, in order to take into account the rearrangement of electronic charge among the layers. These perturbations are introduced in a consistent way as discussed below.

Having defined the tight-binding Hamiltonian, we obtain the electronic band structure and the charge at each layer by using the procedure developed in Ref. 19. In summary, our method uses a Green's-function approach and calculates, by means of a decimation technique, the surface components of the Green's function of the system. Then, we project the whole Green's function onto a few layers around the interface. In our actual case, we have projected the bulk structure of each semiconductor onto its last two layers. In this way, we reduce the whole Hamiltonian to an effective one, associated with two layers of ZnSe, two layers of Ge, and one intralayer (if any) of Al. This yields a 50×50 effective matrix for the case of an intralayer, and a 40×40 matrix for an ideal interface. From these matrices, we can obtain the interface electronic structure.

Consistency has been introduced by considering the electrostatic potential created by the induced charges at the interface. Induced charges are measured with respect to the unperturbed crystal for ZnSe and Ge, and with respect to 3 electrons per atom for Al; then, the diagonal perturbations V_{-2}, V_{-1}, V_0, V_1, and V_2 (going from ZnSe to Ge through Al) are related to the induced charges per two-dimensional unit cell, δn_i, by the following equations:

$$
\begin{aligned}
V_{-2} &= 0 , \\
V_{-1} &= \alpha d \delta n_{-2} , \\
V_0 &= V_{-1} + \alpha d (\delta n_{-2} + \delta n_{-1}) , \\
V_1 &= V_0 + \alpha d (\delta n_{-2} + \delta n_{-1} + \delta n_0) , \\
V_2 &= V_1 + \alpha d (\delta n_{-2} + \delta n_{-1} + \delta n_0 + \delta n_1) ,
\end{aligned}
\tag{1}
$$

where d is the interlayer distance, assumed to be the same between consecutive layers, and $\alpha = 4\pi/A$, A being the area per two-dimensional unit cell. This approach has been found to give the main electronic properties of the interface.[13–15] Notice that a good approximation to Eqs. (1) is obtained by taking $\delta n_2 \approx \delta n_{-1} \approx \delta n_0 \approx \delta n_1 \approx \delta n_2 \approx 0$: this is the charge neutrality condition which in most cases is a good starting point to analyze the heterojunction properties.[13] In this paper, however, we have calculated the interface properties by using the full conditions given by Eqs. (1). Equations (1) and the interface Hamiltonian (a function of V_i) define completely our problem. Notice that the diagonal perturbations V_i have to be calculated by establishing the consistency between the Hamiltonian (giving the charges δn_i) and Eqs. (1). We also mention that in Eqs. (1) we have assumed the induced charges, δn_i, to be uniformly distributed over the planes. We have estimated the uncertainties associated with this approximation by taking into account the effects of having charges with a finite extension of a nonuniform distribution in

TABLE I. Parameters (in eV) defining the Se-Zn, Ge-Ge, Se-Al, Zn-Al, Ge-Al, and Al-Al interactions and the atomic levels.

	Se-Zn	Ge-Ge	Se-Al	Zn-Al	Ge-Al	Al-Al
V_{ss}	−1.55	−1.70	−1.61	−1.61	−1.68	−1.22
$V_{s_1p_2}$	1.51	2.37	1.83	2.46	2.29	1.32
$V_{s_2p_1}$	2.74	2.37	2.55	1.90	2.37	1.32
$V_{pp\sigma}$	3.75	2.85	3.13	3.13	2.73	2.06
$V_{pp\pi}$	−0.75	−0.82	−0.67	−0.67	−0.70	−0.59
$V_{s_1^*p_2}$	1.12	2.26	1.48	1.83	2.10	1.07
$V_{s_2^*p_1}$	1.71	2.26	1.92	1.56	2.21	1.07

	Se	Zn	Ge	Al
E_s	−11.84	0.02	−3.91	−0.51
E_p	1.51	5.99	3.59	4.24
E_{s^*}	7.59	8.99	8.36	7.38

each layer. We have found these effects to be practically negligible.

In this paper we only present the results for two semi-infinite crystals with and without an Al intralayer; these are the cases of ZnSe-Al-Ge and ZnSe-Ge. Results for different number of Ge layers deposited on ZnSe-Al or on ZnSe will be published elsewhere.

Our calculations yield for V_i the results shown in Table II. In Figs. 2 and 3 we present the local density of states for the different interface layers as calculated for ZnSe-Ge and ZnSe-Al-Ge. The most important result emerging from this calculation is the change in the semiconductor band discontinuity due to the Al intralayer. This is given by the change in V_2 that, according to Table II, amounts to 0.35 eV. Notice that for the ideal ZnSe-Ge heterojunction we find that $\Delta E_V = 1.70$ eV, in reasonable agreement with the experimental evidence[3] (1.40 eV), while for the ZnSe-Al-Ge case, $\Delta E_V = 2.05$ eV. We also mention that we have estimated the error in our result for the change in ΔE_V to be ± 0.1 eV; this has been deduced by analyzing the band-offset changes induced by suitable modifications of the different parameters used in the calculation.

How can the change found in ΔE_V be explained in simple terms? According to the charge-neutrality-level approach[7] the band offset of two semiconductors can be approximately obtained by aligning the charge-neutrality levels of both semiconductors. This is known to yield a good value for ΔE_V in ZnSe-Ge.[20] A naive application of the same approach suggests that ΔE_V cannot change too much when a metallic intralayer is deposited between the two semiconductors, even if corrections due to the high ionicity of ZnSe are included:[7,20] indeed, we expect that the Fermi energy of the metallic intralayer should be located at the same energy as the charge neutrality levels of both semiconductors, in such a way that the charge neutrality levels of the two semiconductors keep their alignment. In this argument it is assumed that the charge neutrality levels of both semiconductors are independent of the metal deposited on the semiconductor surface. Although this assumption can be expected to be a good zeroth-order approximation for low-ionic semiconductors, it must be stressed that the charge neutrality levels show a non-negligible dependence on the metal deposited on the semiconductor and on the geometrical position of those atoms.[21]

Regarding the present calculation, we have found that the deposition of an Al layer between ZnSe and Ge changes the charge neutrality level of both semiconductors. Thus, for Ge the charge neutrality level moves up-

TABLE II. Diagonal perturbations (in eV) on the last ZnSe layer (V_{-1}), on the Al intralayer (V_0) and on the two last layers of Ge (V_1 and V_2). (i) ZnSe-Ge ideal heterojunction (without intralayer). (ii) ZnSe-Al-Ge heterojunction.

	V_{-1}	V_0	V_1	V_2
(i)	−0.06		−0.18	−0.27
(ii)	−0.03	0.46	0.38	0.08

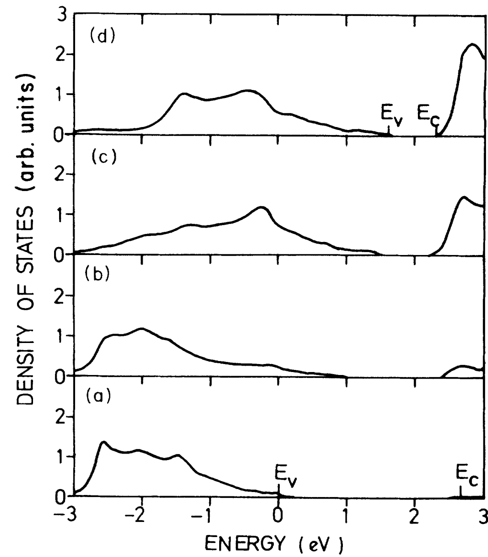

FIG. 2. Local density of states in different layers of the ZnSe-Ge(110) heterojunction. (a) ZnSe layer (−2). (b) ZnSe layer (−1) (interface layer). (c) Ge layer (1) (interface layer). (d) Ge layer (2). E_c denotes conduction-band bottom; E_V denotes valence-band top.

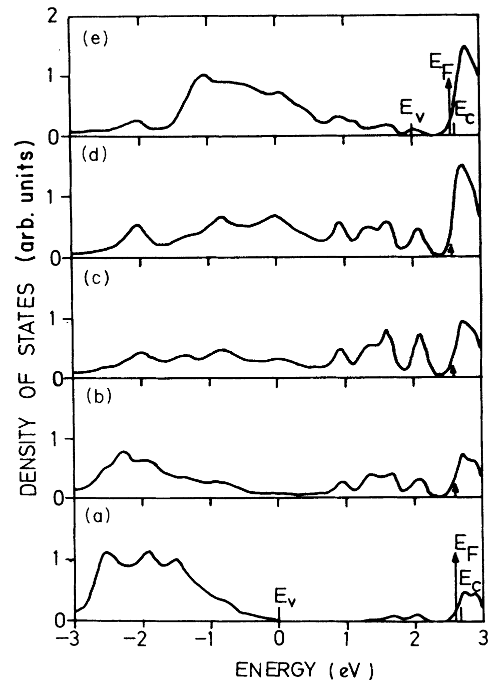

FIG. 3. Local density of states in different layers of the ZnSe-Al-Ge(110) heterojunction. (a) ZnSe layer (−2). (b) ZnSe layer (−1) (interface layer). (c) Al monolayer (0). (d) Ge layer (1) (interface layer). (c) Ge layer (2). E_F denotes Fermi level; E_c denotes conduction-band bottom; E_V denotes valence-band top.

wards in energy by ≈ 0.2 eV, while for ZnSe that shifts amount to ≈ 0.6 eV: the difference between the shifts of the two levels yields, approximately, the change in the valence band discontinuity of ZnSe and Ge.

Finally, we mention that our results are in reasonable quantitative agreement with the results presented by Niles *et al.*[9] who have found a change of 0.2–0.3 eV in ΔE_V under the deposition of a 2 Å thick Al intralayer between ZnSe and Ge. The difference between these results and our theoretical prediction ≈ 0.35 eV is probably due to size effect related to the number of Ge layers deposited at the interface.

In conclusion, we have presented the first theoretical calculation showing that the deposition of an Al intralayer between ZnSe and Ge increases their band offset by ≈ 0.35 eV. This is in good agreement with the actual experimental prediction and shows that an ideal interface is an adequate model to explain the interface behavior. Our results show that the change in the band discontinuity is an effect related to a shift in the charge neutrality levels of both semiconductors induced by the deposited intralayer. We are now currently investigating the effects of other intralayers.

We thank P. Perfetti and G. Margaritondo for drawing our attention to the problem discussed in this paper. We also thank E. M. Godfrin, M. C. G. Passeggi, and G. Allan for their help in the numerical analysis. This work has been partially supported by the Comisión Asesora de Investigación Científica y Técnica (Spain).

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