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〈연구논문〉

The Electronic Properties and the Interface Stoichiometries of Ge-GaAs and AlAs-GaAs

Hwasuck Cho, Jinho Park, Youngkee Oh and Mingi Kim

Department of Physics, Yeungnam University, Gyongsan 712-749, Korea

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Ge-GaAs 계면과 AlAs-GaAs 계면의 전자구조와 화학적 특성

조화석 · 박진호 · 오영기 · 김민기

영남대학교 자연과학대학 물리학과

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Abstract — A method for the calculation of the electronic LDOS is applied to the GaAs-Ge(AlAs) the heterojunction to study the relation of the electronic properties to interface atomic structures of interfaces. The method is based on the tight-binding recursion method. In this paper we propose a convenient way of studying the band-offsets, the interface formation energy, and the bond order of interface bonds from the LDOS across the interface. Conclusively, the band structure is much subordinated to the interface stoichiometry.

요 약 — 계면의 원자구조와 전자특성간의 상관성을 연구하기 위하여 GaAs-Ge(AlAs) 이종접합에서 전자의 국소상태밀도(LDOS)를 계산하였다. 본 연구에서는 tight-binding recursion 방법을 기초로 하여 계면의 국소상태밀도로부터 band-offsets, 계면형성에너지, 계면결합의 bond order 등을 연구하는 보다 편리한 방법을 제시하였다.

1. Introduction

There have been many studies on the physical properties of the Ge-GaAs and of the AlAs-GaAs heterojunction systems, such as the band offsets[1-15], the interface atomic structures[5-9], the electronic properties of interfaces[8-16] and so on.

Since the pioneering work of Schottky in 1939, many different models[1, 4, 15] have been proposed to explain the band-offset formation of semiconductor heterojunctions. In spite of these works, the most realistic theoretical attempts to calculate the band offset at interface have been typically less successful than some simple models[4], and the electronic properties of interface atoms and the atomic structure at interface are not fully explained.

Experimentally, the electronic structure, the local density of states (LDOS), and the bonding properties at the interfaces have been studied using the ultraviolet photoemission and the X-ray photoemission spectroscopy.

The LDOS calculations at the interfaces of GaAs and the other semiconductors, such as Ge and AlAs, are used to interprete the above spectroscopic data.

The Haydock recursion method[17a] is ideally suited to study the local electronic properties at the interfaces. From this method, we can directly compute the LDOS, the partial LDOS[17a, 17b], the integrated LDOS[17a, 17b] and the band structure (BS) energy[17a, 17c]. Using these quantities we can study the local bonding properties, such as the bond order[17a, 17d], the formation energy[7, 17a] and so on.

Let us consider the heterojunction of the semico-

nductors #1 and #2. Here, the semiconductor #1 and #2 consists respectively of the atoms *A*, *B* and *C*, *D*.

2. Calculations

The electronic band structure of each semiconductor is described by means of a tight-binding model, using sp^3s^* basis in each atom, and including interaction parameters that extend up to first neighbors.

The parameterized hamiltonian can be expressed as the sum of the on-site and the hopping parameter. Using the fitting method, we can obtain the bulk hamiltonians of both semiconductors from the published band structure result[8].

However, at the interface of a junction, we can no longer use the fitting method. The reason for this is that there is no pseudopotential results for the semiconductor consisting of *A* and *C*, for example, GeAs. Therefore, we express the hopping parameters between the electronic states of the atoms *A* and *C* as

$$V(\alpha:A,\beta:C)=\sqrt{V^{\circ}(\alpha:A,\beta:B)\times V^{\circ}(\beta:C,\alpha:D)}\times S_{AC} \quad (1)$$

Here, S_{AC} represents the atomic bond order between α orbital of *A* atom and β orbital of *C* atom;

Table 1. Hamiltonian parameters (unit: eV)

Hopping parameters		GaAs						AlAs						Ge		
		Ga			As			Al			As			Ge		
		s	p	s*	s	p	s*	s	p	s*	s	p	s*	s	p	s*
GaAs																
Ga	s				−1.68	2.32					−1.67	2.35		−1.48	2.05	
	pσ					2.83	1.61					2.72	1.64		2.49	1.96
	pπ					−0.81						−0.70			−0.71	
	s*					1.89						1.64			1.96	
As	s	−1.68	2.63					−1.67	2.41					−1.90	2.81	
	pσ		2.83	1.89					2.72	1.64					3.20	1.96
	pπ		−0.81						−0.70						−0.92	
	s*		1.61						1.64						1.96	
AlAs																
Al	s				−1.67	2.26					−1.67	2.38				
	pσ					2.27	1.64					2.62	1.67			
	pπ					−0.70						−0.60				
	s*					1.64						1.62				
As	s	−1.67	2.50					−1.67	2.21							
	pσ		2.72	1.64					2.62	1.62						
	pπ		−0.70						−0.60							
	s*		1.64						1.67							
Ge																
Ge	s	−1.48	2.19		−1.90	2.64								−1.70	2.37	
	pσ		2.49	1.96		3.20	1.96								2.85	1.56
	pπ		−0.71			−0.92									−0.82	
	s*		1.96			1.96									1.56	

On-site parameters	GaAs		AlAs		Ge
	Ga	As	Al	As	
E_s	−11.37	−18.00	−13.10	−18.40	−15.00
E_p	−4.90	−8.98	−7.11	−9.38	−7.51
E_s^*	−3.99	−2.13	−2.67	−0.83	−2.73

0.875[19] and 1.125 for Ga-Ge and Ge-As bonds respectively. $V^{\circ}(\alpha : A, \beta : B)$ and $V^{\circ}(\beta : C, \alpha : D)$ represent the bulk hopping parameters of the hamiltonian for each semiconductor. The used parmaters for Ga-As, Al-As, Ge-Ge, Ge-As bonds are shown in Table 1.

In previous researches, the arithmatic average [12], geometric mean, and d^{-2} scaling law[8] were usually adapted to interface calculation but these corrections could not well accounted for the characteristics of interface (IF) bonds. Therefore, we used a new estimation, Eq. (1), for additional interface chemical bonds, the calculated values for hopping parameters from ours (Table 1) and from geometric mean (reference 8) are not far from each other and the diffenrence is not crucial.

The Haydock recursion method has been extensively discussed elsewhere. Calculation were done with 20 levels continued fraction coefficients, and lattices containing 1570 atoms which were spherically coordinated. The lattice of spherically coordinated 1570 atoms has shown no significant differences in LDOS curves and the integrated quantitites (Fermi level, integrated LDOS and BS energy) from the lattice contained more than 3000 atoms which were coordinated cubically. The lattice size is much important in calculation, because the size is directly correlated with computing times and calcuation accuracy.

Due to the small lattice mismatches ~0.1% in both Ge-GaAs and AlAs-GaAs heterosystems which have the smallest mismatch of any known heterojunctions, it is reasonable to ignore the effects of the dislocations and the faceting.

For the Ge/GaAs heterojunction (the prototype of lattice matched heterovalent system[7] in which the ionicity changes from zero to a positive value across the IF), there are three types of IF atomic structures. One is (001) Ge-As IF is constructed between ideal (001) Ge surface and ideal (001) As-terminated GaAs surface, the IF bond is only Ge-As bond. Another is (001) Ge-Ga IF in which there is only Ge-Ga bond. The other is (110) Ge-GaAs IF where there are equal numbers of Ga-Ge bonds. The (001) planes of atoms in zinc-blend structure are polar, meaning that alternate planes are composed completely of metal atoms or completely of nonmetal atoms, but the (110) plane is nonpolar in which has equal numbers of metal and nonmetal atoms are.

For the AlAs-GaAs heterojunction (the prototype of lattice matched isovalent system[7] the IF atomic structures are also three kinds. The first is (001) Ga-As IF where the IF is constructed between ideal (001) Ga-terminated GaAs surface and ideal (001) As-terminated AlAs surface, and the IF bond Ga-As bond will be different form the corresponding bond in the bulk GaAs. The second is (001) As-Al IF where the IF is constructed between ideal (001) As-terminated GaAs surface and ieal (001) Al-terminated AlAs surface, and the IF bond As-Al bond also will be different from the corresponding bond in the bulk AlAs. The third is (110) AlAs-GaAs IF where there are equal numbers of Ga-As and As-Al bonds which constructed between nonpolar (110) AlAs surface and nonpolar (110) GaAs surface.

3. Results

3.1. Ge-GaAs

The spectrum of LDOS for Ge-GaAs IF are shown in Fig. 1 to Fig. 3 together with the corresponding bulk LDOS. Fig. 1 shows LDOS for GaAs and Ge at (110) IF. Fig. 2 displays LDOS for As at (001) As-Ge IF, while Fig. 3 shows LDOS for Ga at (001) Ga-Ge IF.

Interface localized states are shown in a amall frame on Fig. 1(a), if positive, the LDOS exceeds the corresponding bulk state densities.

We found six types (bands) of IF states in the valence-band energy region. All IF states lie very near bulk band or lie overlapping with bulk band. The IF localized states (A_1, A_2, A_3) of the Ge-As IF appeared below the corresponding bulk states, and the IF localized states (C_1, C_2, C_3) of the Ge-Ga IF occured above the bulk bands from which they were derived. The character of six IF localized states are summarized in Table 2.

It is apparent from the Figs. 1~3 that the Ge-As and Ge-Ga bonds are significantly different from the Ge-Ge or Ga-As bonds.

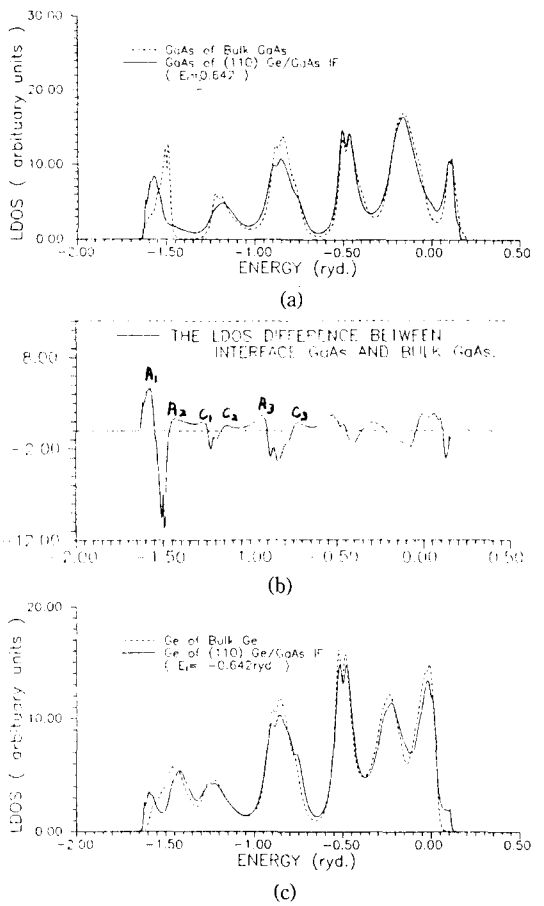

Fig. 1. (a) The full line denotes the LDOS of GaAs located at (110) Ge/GaAs interface and the dot line denotes the LDOS of GaAs located in bulk. (b) The LDOS difference between the LDOSs for GaAs at (110) Ge/GaAs interface and bulk GaAs. (c) The full line denotes the LDOS of Ge located at (110) Ge/GaAs interface, and the dot line denotes the LDOS of Ge located in bulk.

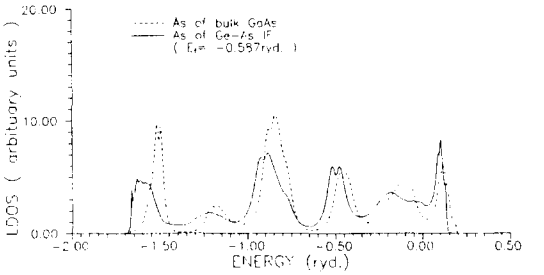

Fig. 2. The LDOS of As at (001) Ge-As interface (full line) and the LDOS of As bulk GaAs (dot line).

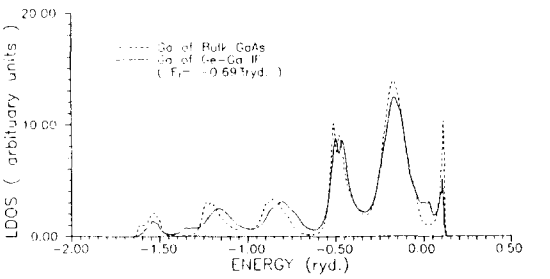

Fig. 3. The LDOS of Ga at (001) Ge-Ca interface (full line) and the LDOS of Ga bulk GaAs (dot line).

Table 2.

	Characteristic bond
A_1	s orbital(Ge) – s orbital(As)
	p orbital(Ge) – s orbital(As)
A_2	s orbital(Ge) – s orbital(As)
A_3	p orbital(Ge) – p orbital(As)
C_1	s orbital(Ge) – s orbital(Ga)
C_2	s orbital(Ge) – s orbital(Ga)
	p orbital(Ge) – s orbital(Ga)
C_3	s orbital(Ge) – p orbital(Ga)
	p orbital(Ge) – p orbital(Ga)

This behavior can be also roughly estimated from the following simple chemical consideration. Since (Ga, Ge, As) atoms have (3, 4, 5) valence electrons (e s) to their tetrahedral bonds, they contribute (0.75, 1.00, 1.25) e s per bond. This leads to an initial estimate of 1.75 and 2.25 e s for the Ge-Ga and Ge-As bonds.

We have calculated the total density of states in various bonds to check the applicability of this argument. Whereas each bond in bulk contains 2 e s. we obtained that the Ge-Ga and Ge-As bonds across the IF contain 1.89 e s and 2.11 e s, respectively. Thus the states densities at this IF are noticeably more uniform than simple consideration would indicate. In our calculations the charge transfer occurs between atomic layers adjacent to each interface, and the IF states for polar IF appeared in the gap. But in the case of (110) interface, as like Pickett *et al.*[8, 12, 16] presented, the interface states density is too small to make any contribution to the density of states in the form of separate

Table 3. Interface atoms electron occupancy change from bulk

Ge-GaAs (001)	
Our Results	
bond	
ΔQ=s(−0.03)p(−0.07): Ge − As:	ΔQ=s(−0.03)p(−0.20)
ΔQ=s(+0.06)p(+0.16): Ge − Ga:	ΔQ=s(+0.04)p(+0.01)
Reference 10	
ΔQ= −0.42: Ge − As:	ΔQ= −0.38
ΔQ= +0.42: Ge − Ga:	ΔQ= +0.38
AlAs/GaAs (110)	
Our Results	
bond	
ΔQ=s(+0.00)p(+0.04): Al − As:	ΔQ=s(−0.01)p(−0.20)
ΔQ=s(+0.01)p(+0.15): As − Ga:	ΔQ=s(−0.00)p(−0.04)
Reference 11	
ΔQ=s(−0.02)p(−0.06): Al − As:	ΔQ=s(−0.02)p(−0.12)
ΔQ=s(+0.03)p(+0.12): As − Ga:	ΔQ=s(+0.02)p(+0.06)

peaks.

From Figs. 2 and 3 we found that Ge-As(Ge-Ga) bonds represent a sheet of occupied (empty) states below (above) conduction (valence) band bottom (top) which have donor (acceptor) character in bulk semiconductor and can give (accept) up to 0.5 e s per IF atom based on the simple chemical consideration. These behavior of polar IF is the same that occurs in ideal polar surfaces of GaAs. In our calculation the amount of donor (acceptor) state is 0.26 e s (0.1 e s) which is much less than 0.5 e s and the IF state density at the Fermi level is (0.03 states/atom·ryd) and (0.15 states/atom·ryd) for (001) IF As and (001) IF Ga, respectively. While Fermi level is located about 0.7 eV (0.7 eV) above (below) the Ge valence band edge for (001) Ge-As (Ga-Ge) IF, and Fermi level is 0.03 eV below Ge valence band edge for nonpolor (110) IF. It is comparable with the results of Pollmann *et al.*[12] of Fermi level of Ge-Ga interface to be about 0.55 eV below the top of the Ge bulk valence bands.

As shown in Table 3, because of the lack of translational symmetry perpendicular to the IF, there is not the same charge on each layer any longer. From less electronegative side to more electronegative one, the charge is transfered. Using the transfered charge, we obtained interface dipole potential with average dielectric constants.

The valence band offsets are obtained as sum of band-edge difference[10, 15] (in our calculation, the valence band edge difference is 0.33 eV for Ge-GaAs hetero-IF) and the calculated IF dipole potential. Therefore the valence-band offsets, i.e., barriers between Ge side and GaAs side, are 0.45 eV, 0.21 eV and 0.55 eV for nonpolar (110), polar (001) Ge-As and polar (001) Ge-Ga IF, respectively. Our ΔE_v=0.45 eV for nonpolar (110) IF is in good agreement with the experiments[3, 5, 9] and the previous calculations[6, 7, 12, 15, 16] with some exceptions[15].

From the band structure (BS) energy difference between the BS energies[17b] of the interface atoms and the corresponding bulk atoms, we obtained the interface formation energy expressed as,

$$\Delta E = E(\text{Ge-GaAs}) - [E^{\circ}(\text{GaAs})] \quad (2)$$

where the first term defines the BS energy for interface unit cell and the second term represents the corresponding bulk BS energy of Ge and GaAs.

The ideal polar IF is less stable than the nonpolar (110) IF as shown Table 4, and Ge-Ga IF is more unstable than Ge-As IF as known in references 5~7. Therefore the IF stability is much correlated with the IF atomic structure and IF stoichiometry, i.e., the (Ge-As/Ga-Ge) ratio.

When we include the exchange of the interface atoms, a more attractive IF will be obtained. Such a mixed polar IF will be similar to that of the bonds at nonpolar Ge-GaAs (110) IF, this prediction is well cosistent with experiments[5, 20].

From the partial LDOS of IF atom, we show fact that Ge's-orbital has three distinct bands which are induced from the difference of Ga-Ge, Ge-Ge and Ge-As bond strengths.

3.2. AlAs-GaAs

The LDOS for AlAs-GaAs IF oriented (001) direction are shown in Figs. 4 and 5 together with corresponding bulk LDOS, where Fig. 4 shows the LDOS for IF As at (001) Al-As IF and Fig. 6 shows the LDOS for IF As at (001) Ga-As IF. The LDOSs for AlAs and GaAs of (110) IF don't show any signi-

Table 4.

	IF formation energy (meV/2 atoms)
Ge-As (001)	33.0
Ge-Ga (001)	74.0
Ge/GaAs (110)	30.0
AlAs/GaAs (001) (Al-As IF)	109.0
AlAs/GaAs (001) (Ga-As IF)	80.0
AlAs/GaAs (110)	21.0

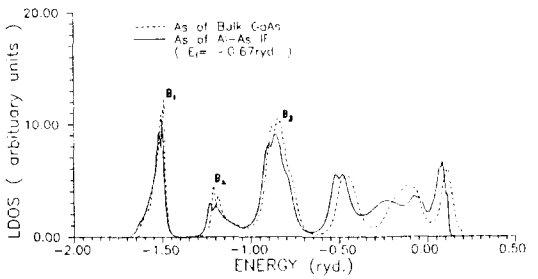

Fig. 4. The LDOS of As at (001) Al-As interface (full line) and the LDOS of As bulk GaAs (dot line).

ficant changes from the corresponding bulk LDOS (not shown). As shows in Figs. 4 and 5, there is small difference in IF LDOS from bulk. Perhaps the most important results are that IF states do occur in Ge-GaAs but do not occur in AlAs-GaAs. The IF bond strength differences of Al-As bond of Al-As IF, and Ga-As IF from those of Al-As bond in bulk AlAs and Ga-As in bulk GaAs are represented in the LDOS of Figs. 4 and 5 the LDOS of IF As of Al-As IF is shifted down-ward on X-axis, and that of Ga-As IF is shifted up-ward[11, 13]. These shifts of three IF bands (B_1, B_2, B_3) from the corresponding bulk bands are 0.1 eV, 0.2 eV and 0.2 eV for Al-As IF and 0.0 eV, 0.15 eV and 0.35 eV for Ga-As IF and for the same IF Schulman and McGill [11] calculated that the shift of (B_1, B_3) is 0.1, 0.15 eV for former IF and 0.1, 0.2 eV for latter IF where B_2 was not detected.

The integrated LDOS of As at Al-As IF is less 0.2 e^-s than that of As in bulk GaAs and the integrated LDOS of As at Ga-As IF is more 0.18 e^-s than that of As in bulk AlAs, while the amount of transfered e from GaAs for all three IF is about

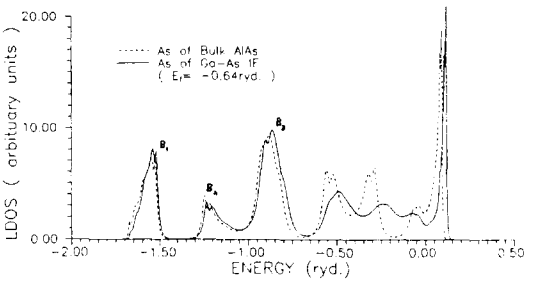

Fig. 5. The LDOS of As at (001) Ga-As interface (full line) and the LDOS of As bulk AlAs (dot line).

0.2 e which is similar to the Ge-GaAs.

For IF formation energy, the nonpolar IF formation energy is positive 21 meV (which is less than in heterovalent Ge-GaAs, 30 meV). The IF formation energys in our calculation for all IF are positive like the recent results[14, 21, 22], much larger in polar IF than nonpolar IF and much largr in Ge-GaAs than AlAs-GaAs, hence these ideal hetero-IF are unstable thermodynamically and IF atom's diffusion and IF atom's exchange may be occured.

The valence band offset is calculated as sum of band-edge difference, 0.04 eV and the IF dipole potential, therefore the obtained valence band offsets are 0.56 eV, 0.53 eV, 0.56 eV for nonpolar (110) and Al-As IF and Ga-As IF of AlAs/GaAs heterojunction, respectivily. Our valence band offset, 0.56 eV, is larger than published results 0.45 eV of Bylander *et al.*[14], and experiment[2].

4. Conclusions

(1) Our parameter scallings is reasonable in the interface calculation judging from which we calculated LDOSs and integrated quantities.

(2) The polar IF of Ge-GaAs (heterovalent junction) has impurity band gap.

(3) Generally, heterojunction IF is unstable, and the polar is more unstable than nonpolar and Ge-GaAs IF (heterovalent) is more unstable than AlAs-GaAs IF (isovalent). When we include the influence of the lattice relaxation, interface diffusion and the on-site parameters correction for interface atoms, we will obtain a more attractive results.

(4) From our results, we know that even lattice

matched heterojunction have unique interface stoichometry.

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19. A bond order is obtained by the number of valence electron. For example, the bond order of Ge-Ge is $1=\{(4+4)/4\}2$ of Ga-As is also $1=\{(3+5)/4\}2$ and of Ga-Ge is $0.875=\{(3+4)/4\}2$ the numerators are the number of valence of bonding atoms and 4 in the denominator is number of bonding for each atoms.
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