

# Transient of Electrostatic Potential at GaAs/AlAs Heterointerfaces Characterized by X-Ray Photoemission Spectroscopy

XPS 法による GaAs/AlAs ヘテロ界面における遷移領域の評価

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平川一彦・橋本佳男・生駒俊明

We systematically studied the Ga3d and Al2p cation core level binding energies in molecular beam epitaxially grown GaAs/AlAs heterostructures by in-situ x-ray photoemission spectroscopy. The valence band offset  $\Delta E_v$  at GaAs/AlAs interface is found to be  $0.44 \pm 0.05$  eV. Furthermore, we found that the cation core level binding energies in the extreme vicinity of the interface are shifted by  $\sim 0.1$  eV from their respective bulk values, which clearly indicates that the charge distribution and the resulting band offsets have a transient over a distance of at least  $\pm 2$  monolayers from the heterointerface.

## 1. INTRODUCTION

The band offset at semiconductor heterojunctions has been a topic of technological as well as physical interests. Most of the model theories for heterojunction band offsets (HBOs) predict that HBOs are given by the difference in the energy positions of the band extrema in the two constituent *bulk* semiconductors measured from an *appropriate reference level*, such as the vacuum level<sup>1)~3)</sup> or the charge neutrality level<sup>4)~6)</sup>, although each of these theories stands on a very different physical point of view. The experimental result of the orientation independence of the HBO at GaAs/AlAs interfaces, which will be also presented in this paper, seems to further support this idea. Then, we can raise a question about how abruptly the band extrema change in the interface region. So far, microscopic details of the valence charge density and the resulting electrostatic potential in the heterointerface regions have not been studied experimentally.

In this work, we systematically studied the core level binding energies of Ga3d and Al2p core levels,  $E_{\text{Ga3d}}$  and  $E_{\text{Al2p}}$ , in molecular beam epitaxially (MBE) grown GaAs/

AlAs heterostructures by in-situ x-ray photoemission spectroscopy (XPS). We found that the valence band offset  $\Delta E_v$  at GaAs/AlAs interfaces is  $0.44 \pm 0.05$  eV, independent of the crystallographic orientation. Furthermore, we measured  $E_{\text{Ga3d}}$  and  $E_{\text{Al2p}}$  as a function of the distance from the heterointerface. It is found for the first time that  $E_{\text{Ga3d}}$  and  $E_{\text{Al2p}}$  in the extreme vicinity of the interface are shifted by  $\sim 0.1$  eV from their respective bulk values, which clearly indicates that charge distribution and the resulting electrostatic potential have a transient of at least  $\pm 2$  monolayers (MLs) from the interface. We will discuss how abruptly the HBOs are established at the heterointerfaces.

## 2. ORIENTATION INDEPENDENCE OF HETEROJUNCTION BAND OFFSETS

Because the tetrahedral bond configurations are strongly dependent on the crystallographic orientation, to check the face dependence of HBOs is very informative about the origin of HBO. We systematically studied the valence band offset  $\Delta E_v$  at lattice matched GaAs/AlAs (100), (110), and (111) B heterojunctions.

GaAs/AlAs heterojunctions were grown on (100), (110), and (111) B GaAs substrates by MBE. Each of the AlAs-on-GaAs interfaces was prepared by growing successively a 3000 Å-thick Si-doped *n*-type GaAs buffer layer and a 30 Å-thick undoped AlAs layer on an *n*-type GaAs

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substrate. The reversed GaAs-on-AlAs structure consists of a 3000 Å-thick *n*-type GaAs buffer layer, a 100 Å-thick undoped AlAs layer, and a 30 Å-thick GaAs capping layer. The Si-doping density was set to be  $1 \times 10^{16} \text{ cm}^{-3}$ . To obtain mirror surfaces, special care was taken in the MBE growth on the (110) and (111) B faces, which will be reported elsewhere.<sup>7</sup> For the (110) orientation we inserted a 600 Å-thick undoped InAs buffer layer between the (110) GaAs substrate and the epitaxial overlayer.<sup>8</sup> For the (111) B orientation, we used the (111) B substrates which are 2°-misoriented toward the (100) orientation.<sup>9</sup> The samples were immediately transferred to the analysis chamber via an ultrahigh vacuum transfer tube. This experimental configuration eliminates experimental uncertainties arising from surface contaminations. XPS measurements were performed by using monochromatic Al K $\alpha$  x-ray ( $h\nu = 1486.6 \text{ eV}$ ) as an excitation source. The analyzer pass energy was set to be 20 eV.

Since the energy resolution of XPS measurement ( $\sim 0.7 \text{ eV}$  under the present experimental condition) is not enough to resolve two valence band edges in heterojunctions, deep core levels are used as markers (see Fig. 1). The valence band offset  $\Delta E_V [\equiv E_V(\text{GaAs}) - E_V(\text{AlAs})]$  is determined from XPS measurements as the following;

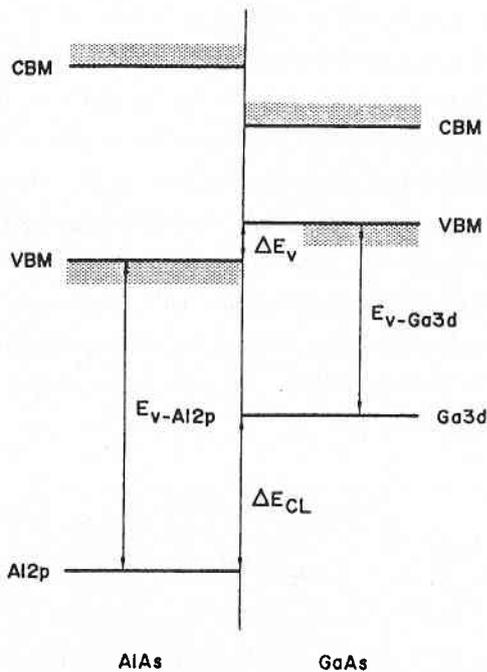


Fig. 1 A schematic energy band diagram at GaAs/AlAs heterojunctions.

$$\Delta E_V = E_{V-\text{Ga}3d} - E_{V-\text{Al}2p} + \Delta E_{\text{CL}}, \quad (1)$$

where  $\Delta E_{V-\text{Ga}3d}$  and  $\Delta E_{V-\text{Al}2p}$  are the core level binding energies relative to the valence band maxima (VBM) in the bulk GaAs and AlAs and were determined to be  $18.83 \pm 0.05 \text{ eV}$  and  $72.80 \pm 0.05 \text{ eV}$ , respectively, from separate experiments on bulk samples. Since  $E_{V-\text{Ga}3d}$  and  $E_{V-\text{Al}2p}$  are the quantities specific to the constituent bulk materials, all the information on the band lineup is contained in  $\Delta E_{\text{CL}}$ . Therefore, we can discuss the face dependence of  $\Delta E_V$  by measuring the face dependence of  $\Delta E_{\text{CL}}$  systematically.

A typical XPS spectrum taken on an AlAs-on-GaAs heterojunction grown on (110) GaAs is shown in Fig. 2. We made at least two independent experiments for each type of heterostructures. Table I summarizes the obtained values of  $\Delta E_{\text{CL}}$  for different orientations and growth sequences. It was found that  $\Delta E_{\text{CL}}$  depends neither on the substrate

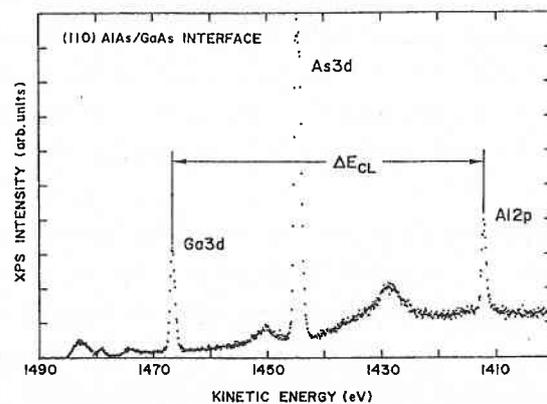


Fig. 2 A typical XPS spectrum measured on an AlAs-on-GaAs (110) heterojunctions.  $\Delta E_{\text{CL}}$  is the energy difference between Ga3d and Al2p core levels.

Table I The core level energy difference  $\Delta E_{\text{CL}}$  between Ga3d and Al2p levels measured for GaAs/AlAs heterojunctions with various crystal orientations and growth sequences. Experimental uncertainty is  $\pm 0.03 \text{ eV}$ .

Orientation	Growth Sequence	$\Delta E_{\text{CL}}$ (eV)
(100)	GaAs on AlAs	54.41, 54.42
	AlAs on GaAs	54.42, 54.42
(110)	GaAs on AlAs	54.41, 54.42
	AlAs on GaAs	54.42, 54.42
(111)B	GaAs on AlAs	54.40, 54.40
	AlAs on GaAs	54.42, 54.39

orientation nor on the growth sequence and is constant to be  $54.41 \pm 0.03$  eV within the experimental uncertainty, which clearly indicates the face independence of  $\Delta E_V$ . By substituting the obtained values of  $\Delta E_{CL}$  into Eq. (1),  $\Delta E_V$  is determined to be  $0.44 \pm 0.05$  eV, which is in good agreement with the results of recent ab-initio self-consistent band calculations.<sup>3),10)~12)</sup>

### 3. CHARGE DISTRIBUTION IN THE EXTREME VICINITY OF HETEROINTERFACES

Our experimental evidence of face independence of  $\Delta E_V$  strongly suggests that HBO is determined by the *bulk* properties of the two constituent materials which from a heterojunction. Therefore, we can draw a schematic energy band diagram, as shown in Fig. 3. In the figure shown are the common reference energy level, the energy positions of valence band maxima (VBM) and the unit cell-averaged electrostatic potential due to valence electrons and ionized cores. Then, how abruptly do the properties which are relevant to determine HBOs, such as the valence electron density and/or the electrostatic potential, change at the interface? In other words, how thick is the transient layer which are necessary for HBOs to be established?

In order to clarify this, we traced the shift of the electrostatic potential in the crystal as a function of the distance from the interface by measuring the shifts of the cation core level binding energies,  $\Delta E_{V-Ga3d}$  and  $\Delta E_{V-Al2p}$ , since the shift of cation levels corresponds to the shift in the electrostatic potential on the cation sites. (In the following, we will simply call this core level binding energy shift "interfacial chemical shift".) If the valence electron density changes from that in the bulk GaAs to that in the bulk AlAs abruptly within a Wigner-Seitz cell at the interface, then  $\Delta E_{V-Ga3d}$  and  $\Delta E_{V-Al2p}$  should be *position independent*.<sup>13)</sup> However, if the spatial extent of the wavefunction of electrons in the valence shell is larger than the size of the Wigner-Seitz cell and the valence electron density changes gradually over a finite distance, then  $\Delta E_{V-Ga3d}$  and  $\Delta E_{V-Al2p}$  in the vicinity of the interface are expected to be *shifted* from their bulk values. Therefore, by checking the position dependence of  $\Delta E_{V-Ga3d}$  and  $\Delta E_{V-Al2p}$ , we can get information on the microscopic charge distribution in the interface region.

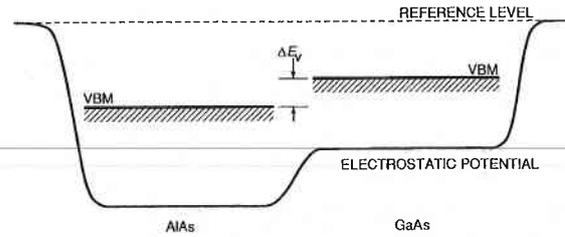


Fig. 3 A schematic energy band diagram at GaAs/AlAs heterojunctions. The broken line denotes the common reference energy level, with respect to which all the energy positions are measured. The solid line is the electrostatic potential generated by the valence electrons and the ionized cores. Note in the figure that the electrostatic potential is continuous across the heterojunction.

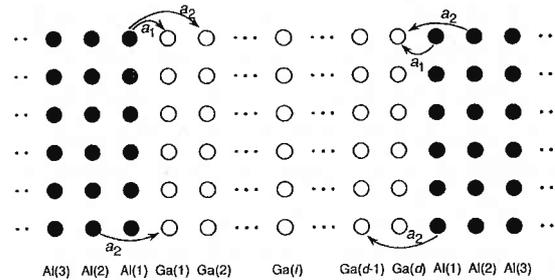


Fig. 4 Cross section of the AlAs/*d*-ML GaAs/AlAs double heterostructure used in determining the interfacial chemical shift of Ga3d core level. In the figure, As atoms are omitted for simplicity.  $a_1$  and  $a_2$  are defined in the text.

Interfacial chemical shifts of the Ga and Al core levels can be determined by measuring  $\Delta E_{CL}$  on AlAs/GaAs/AlAs (GaAs inserted) and GaAs/AlAs/GaAs (AlAs inserted) double heterostructures (DHs), respectively.<sup>14)</sup> For example, Ga3d chemical shift can be determined in the following way. Figure 4 shows the cross section of a AlAs/*d* ML-thick GaAs/AlAs DH. In this structure, the AlAs capping layer is thick enough and, therefore, the XPS signal from AlAs is dominated by the signal from the "bulk" layer. Then, by taking into account the exponential weighting function due to the electron escape depth  $\lambda_e$  ( $\lambda_e \sim 25 \text{ \AA}$  under the present experimental condition), the core level energy distance  $\Delta E_{CL}$  is given by;

$$\Delta E_{CL} = \frac{\sum_{i=1}^d E_{Ga3d}(i) \exp(-\frac{ia_0}{\lambda_e})}{\sum_{i=1}^d \exp(-\frac{ia_0}{\lambda_e})} - E_{Al2}^{bulk}, \quad (2)$$

where  $E_{Al2}^{bulk}$  denotes the bulk Al2p binding energy and  $\Delta E_{Ga3d}(i)$  the Ga3d core level binding energy in the Ga atoms on the *i*-th cation plane from the interface.  $a_0$  is the

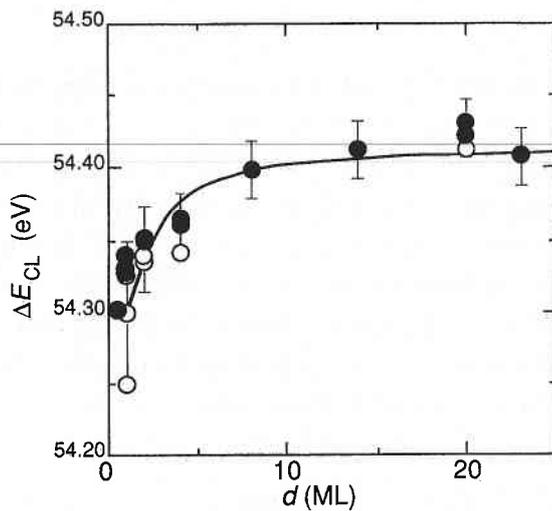


Fig. 5 The core level energy difference  $\Delta E_{CL}$  as a function of inserted layer thickness  $d$ . Full circles denote the data from GaAs-inserted DHs and open circles denote those from AlAs-inserted DHs. The solid line is the fitting curve obtained when  $a_1=35$  meV and  $a_2=25$  meV.

distance between two cation planes (for example,  $a_0=2.83$  Å for GaAs and AlAs (100) planes). If the Ga3d binding energy of the Ga atoms in the "interface" layer is shifted from that of Ga atoms in the inner "bulk" layer,  $\Delta E_{CL}$  is expected to change with  $d$ .

We performed XPS measurements on the AlAs/GaAs/AlAs (GaAs inserted) DHs and the reversed GaAs/AlAs/GaAs (AlAs inserted) DHs grown on (100) GaAs substrates by MBE. Each of the GaAs inserted DH samples consists of a 1  $\mu\text{m}$ -thick  $n^-$ -GaAs buffer layer, a 100 Å-thick undoped AlAs layer, a 0.5-20 ML-thick GaAs inserted layer, and a 30 Å-thick undoped AlAs capping layer, while the AlAs inserted DH sample consists of an  $n^-$ -GaAs buffer, a 1-20 ML-thick AlAs inserted layer, and a 30 Å-thick GaAs capping layer. Since the growth rate was calibrated by the reflection high energy electron diffraction (RHEED) oscillation effect, the uncertainty in the inserted layer thickness is less than 10%.

We systematically measured the core level energy distance  $\Delta E_{CL}$  as a function of inserted layer thickness  $d$ . In Fig. 5,  $\Delta E_{CL}$  measured on the DH samples are plotted as a function of  $d$ .  $\Delta E_{CL}$  measured on both types of DH samples falls on a single curve and increases gradually from  $54.30 \pm 0.05$  eV to  $54.42 \pm 0.02$  eV with increasing  $d$  from 1 to 20 MLs. This indicates that the Ga3d core level

becomes  $\sim 0.1$  eV-deeper by going closer to the interface, while the Al2p level becomes shallower by the same amount. This energy shift clearly indicates that the charge distribution at the cation site in the vicinity of the heterointerface is affected by the presence of the different cation species on the next cation plane and that the electrostatic potential in the crystal gradually changes from the value in the bulk GaAs to that in the bulk AlAs over a finite distance.

In order to determine the magnitude of the interfacial chemical shift as a function of a distance from the interface, we made a simple theoretical fit by Eq. (2) to the experimental data shown in Fig. 5. Our model for the interface chemical shift is very simple; let us consider the case of AlAs/GaAs/AlAs DH, for example. We denote the chemical shift of Ga3d level induced by the  $i$ -th Al plane from the Ga plane of interest by  $a_i$ . Then, the Ga3d chemical shifts for  $j$ -th Ga plane,  $\delta E_{Ga3d}(j) [=E_{Ga3d}(j) - E_{Ga3d}^{bulk}]$ , are given by (see Fig. 4);

$$\delta E_{Ga3d}(1) = 2(a_1 + a_2 + a_3 + \dots); \quad \text{for } d = 1 \text{ ML} \quad (3.1)$$

$$\delta E_{Ga3d}(1) = \delta E_{Ga3d}(2) = a_1 + 2(a_2 + a_3 + \dots); \quad \text{for } d = 2 \text{ MLs} \quad (3.2)$$

$$\delta E_{Ga3d}(1) = \delta E_{Ga3d}(3) = a_1 + a_2 + 2(a_3 + a_4 + \dots), \text{ and} \\ \delta E_{Ga3d}(2) = 2(a_2 + a_3 + \dots); \quad \text{for } d = 3 \text{ MLs} \quad (3.3)$$

and so on. The use of this simplified picture of the interfacial shift is considered to be valid, considering the fact that atomic sphere superpositions is a good approximation in the band structure calculation.<sup>3)</sup>

By substituting Eqs. (3) into Eq. (2) and fitting it to experimental data shown in Fig. 5, we can determine  $a_1$ ,  $a_2$ , etc. If we assume  $a_i (i \geq 3) \approx 0$ , then the best fit is obtained when  $a_1 = -35 \pm 5$  meV and  $a_2 = -25 \pm 10$  meV. (Although we consider that  $a_i$ 's ( $i \geq 3$ ) are finite, they are expected to be further smaller.) As shown by the solid line in Fig. 5, the agreement between the obtained fitting curve and the experimental data is good. These obtained values of  $a_1$  and  $a_2$  are also consistent with the result of chemical shifts of cation cores in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys, which will be reported elsewhere.<sup>15)</sup> From the determined values of  $a_i$ , we can

estimate the interfacial chemical shift for a single hetero-junction ( $d \rightarrow \infty$ ). The estimated values are  $\delta E_{\text{Ga3d}}(1) = a_1 + a_2 = -60 \pm 10 \text{ meV}$  and  $\delta E_{\text{Ga3d}}(2) = a_2 = -25 \pm 10 \text{ meV}$ .

The chemical shift for Al2p level were determined in the same manner. The obtained values have the same magnitude but with a reversed sign and are  $\delta E_{\text{Al2p}}(1) = 60 \pm 10 \text{ meV}$  and  $\lambda_{\text{Al2p}}(2) = 25 \pm 10 \text{ meV}$ . The present result indicates that the electrostatic potential and the resulting HBO have a transient over a distance greater than  $\pm 2 \text{ MLs}$  (possibly  $\pm 3 \text{ MLs}$ ) from the interface. This result also implies that it is important to take into account such transient in the electrostatic potential near the interface in predicting the electronic properties of short period superlattices such as  $(\text{GaAs})_1/(\text{AlAs})_1$  and  $(\text{GaAs})_2/(\text{AlAs})_2$

#### 4. CONCLUSIONS

In summary, we systematically studied the Ga3d and Al2p core binding,  $E_{\text{Ga3d}}$  and  $E_{\text{Al2p}}$ , in molecular beam epitaxially (MBE) grown GaAs/AlAs heterostructures by in-situ XPS. We found that the valence band offset  $\Delta E_V$  at GaAs/AlAs interfaces is  $0.44 \pm 0.05 \text{ eV}$ , independent of the crystallographic orientation. Furthermore, we measured  $E_{\text{Ga3d}}$  and  $E_{\text{Al2p}}$  as a function of the distance from the heterointerface and found  $E_{\text{Ga3d}}$  and  $E_{\text{Al2p}}$  in the extreme vicinity of the interface are shifted by  $\sim 0.1 \text{ eV}$  from their respective bulk values, which clearly indicates that the charge distribution and the resulting electrostatic potential have a transient of at least  $\pm 2$  monolayers (MLs) from the interface. Consequently, it is concluded that the thickness of the transient region which is necessary for HBOs to be established is greater than 4 MLs ( $\sim 11 \text{ \AA}$ ).

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