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Local electronic distribution on Al sites at GaAs/AlAs interface

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Abstract. The spectral density of Al p valence states has been analysed by electron-induced soft x-ray emission spectroscopy (EXES) at the GaAs/AlAs interface. Changes with respect to the density of Al states of bulk AlAs are discussed in relation to the densities of states calculated for various ideal systems. A mixing between the valence states of AlAs and GaAs and point defects such as cation–cation wrong bonds and As vacancies have been observed at the interface.

1. Introduction

In a first paper [1] (labelled I), we have shown that the spectral density of Al valence states of single crystal AlAs, obtained by soft x-ray emission spectroscopy induced by electrons (EXES), is in good agreement with the density of states (DOS) calculated with the help of the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method [2]. The radiative decay of an Al 1s core excitonic state has also been observed. As previously mentioned by Carson and Schnatterly [3], EXES is an appropriate method to observe the core excitonic states in insulators and semiconductors. Indeed, in photoabsorption, core excitonic transitions are difficult to resolve from the edge whereas in emission, so long as no high-energy satellite emission is present, these transitions may clearly be seen because they are energetically located in the band gap.

AlAs is widely used in heterostructures such as heterojunctions, quantum wells and superlattices, so that the electron distribution at the interface between this material and other semiconductors is an important parameter and various information on the interface can be deduced from it. As we have shown elsewhere [4], the distribution of valence states at a 'deep' interface between any two materials can be obtained directly by EXES because it is depth selective.

In this paper we report on the Al 3p–1s emission obtained by EXES for aluminium present at the GaAs/AlAs interface; the spectrum is due to the radiative decay of the Al 1s core hole. We discuss the main part of the emission which involves the transition from Al valence states to this hole and we compare it to densities of valence states

Table 1. Growth conditions of samples.

	1	2
Substrate temperature T_S	605 °C	615 °C
Growth rate[a]:		
v(GaAs)	1.5 μm/h	1.38 μm/h
v(AlAs)	0.4 μm/h	0.45 μm/h
As_4 pressure	4.8×10^{-6} Torr	5.5×10^{-6} Torr

[a] Determined from RHEED oscillation experiments.

calculated for a perfect interface and for systems containing various types of point defects. The radiative decay of an Al 1s core excitonic state is also considered.

2. Experiment

The samples were prepared at Laboratoire de Physique du Solide et Energie Solaire (Sophia Antipolis) [5]. They were grown by means of molecular beam epitaxy on a (100) oriented GaAs semi-insulating substrate. A 1000 Å thick buffer layer, a 500 Å thick AlAs layer and a 100 Å thick GaAs layer were successively deposited on the substrate. The interface studied is between the GaAs top layer and the AlAs layer. Two samples were used [6]; their growth conditions are indicated in table 1.

Reflexion high-energy electron diffraction (RHEED) experiments performed on the two samples [7] and depth profile by SIMS of sample 2 show that the AlAs layer does not form a planar surface at the end of growth (i.e. the surface roughness extends over several monolayers). Furthermore, from XPS and AES experiments and a thermodynamical model of surface segregation in III–V heterostructures [8–10] one expects that the GaAs/AlAs interfacial region, where the composition in Al varies from 0 to 1, is about 10 Å thick.

High-resolution soft x-ray emission spectra are obtained by means of the same device as that used in I. The spectral resolution is about 2×10^{-4} and the photon energy is determined to within about ± 0.2 eV. For each sample, the analysis is performed first on the whole layer, then on the interfacial region.

In the first case, the Al 1s core holes are created with 4.3 keV incident electrons. Only electrons having an energy higher than the Al 1s ionization threshold can create an Al 1s core hole. We have evaluated the variation of the incident electron energy in the 500 Å thick AlAs sample after taking into account the 100 Å thick GaAs top layer. Over the energy range considered, the usual energy-range relations are those of Young [11] and Fitting [12]. From both relations, the mean energy of electrons varies between about 4 and 3.2 keV in the AlAs sample, i.e. it is higher than twice the Al 1s threshold energy. In this range, the cross section of the Al 1s hole creation is large giving an intense spectrum.

In the second case, the analysed thickness must be as small as possible, then the energy of electrons incident at the interface must be near the ionization threshold. It is necessary to take into account the energy distribution of electrons after they have gone through the GaAs top layer [13] and only the electrons with an energy higher than E_S

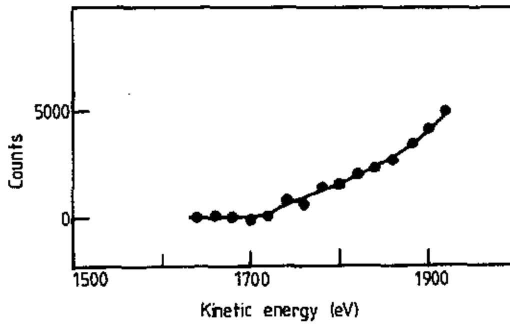

Figure 1. Excitation curve for sample 2 (number of photons in Al 3p–1s emission versus electron energy).

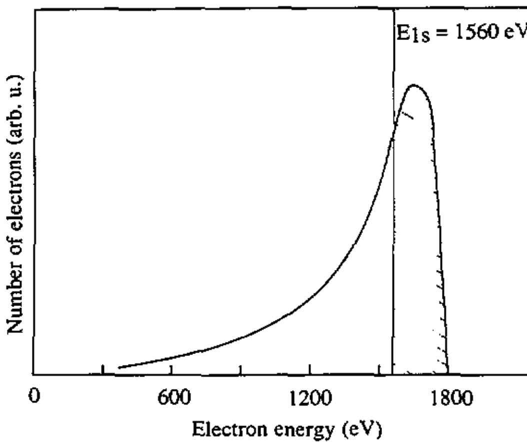

Figure 2. Energy distribution at interface for 1800 eV primary electrons; shaded area represents effective electrons.

are able to create Al 1s core holes (effective electrons). Let E_{max} be the maximum of the distribution: the closer E_{max} is to E_S, the smaller is the thickness analysed at the interface. Using an excitation curve, i.e. a curve corresponding to the number of emitted photons at the energy of the maximum emission and corrected for the background contribution plotted versus kinetic energy of incident electrons E_p, we have determined the apparent threshold of the Al Kβ emission (figure 1). It is about 1700 eV whereas the Al 1s ionization threshold is $\approx$1560 eV. The difference ($\approx$140 eV) between the two values is due to the energy loss of primary electrons in the GaAs top layer. We have recorded the spectrum using E_p = 1800 eV, i.e. 100 eV greater than the apparent threshold.

The electron energy distribution curve depends on the ratio x/R (x is the depth in the sample, R is the practical range of primary electrons). Here x = 100 Å and R is about 500 Å leading to $x/R \approx 0.2$. Figure 2 represents the electron energy distribution at a 100 Å depth in GaAs for 1800 eV primary electrons. It is obtained by transposing to our case the calculation performed by Dejardin *et al* [14] for various materials in the keV energy range. From this curve, the energy of effective electrons is 1660 ± 100 eV at the

interface. The above energy-range relations are not sufficiently precise to make it possible to determine the thickness analysed. The stopping power varies little over the effective energy range (1560–1760 eV). Using its value of about 3 eV/Å for AlAs [15, 16], the analysed thickness is about 30 Å. Indeed, this value is an upper limit because the ionization cross section varies strongly at the threshold and the probability of core level ionization by electrons having the threshold energy is very weak. As a consequence, the region which contributes most to the spectrum is the one closest to the interface; its thickness is between a few Å and about ten Å; it is of the same order as the interfacial zone.

3. Results and discussion

As described in paper I, for bulk single crystal AlAs, Al 3p–1s emission presents three parts, the main peak (I) originating from mainly Al 3p occupied states and two structures (II, III) originating from Al p occupied states mixed with Al 3s and As 4s states respectively (figure 3(a) broken line). A transition is observed from states present in the band gap; its intensity is ≈1% of that of the main emission.

3.1. Valence states

The Al 3p–1s emission at the GaAs/AlAs interface has been studied from both samples; their spectra are identical; experimental dots are shown in figure 3(a) along with the bulk spectrum (broken line). The spectra represent the number of counts versus photon energy; they are normalized with respect to their maximum. An additional scale gives the binding energy relative to the valence band maximum E_V, whose position is determined as in paper I.

Just as for bulk AlAs, the Al p states at the interface spread over all the energy range of the valence band, more or less mixed with other states. Consequently, any change in valence states induces a change in the local p spectral density of states around Al.

Changes are observed in the three regions of valence band going on from bulk AlAs to GaAs/AlAs interface. For peak I, we observe a slight shift towards the higher binding energies (lower photon energies) at the top of the valence band. For II, a clear broadening up to ≈9 eV from E_v is seen at the interface, instead of ≈6.5 eV in bulk AlAs; two structures are present, a broad one at 5.7 eV and another at 7.8 eV from E_v (cf bars on the figure). Lastly, structure III disappears at the interface.

To interpret these changes, we compare our experimental spectra with DOS calculated for various idealized systems. We consider theoretical DOS obtained by different methods; it must be underlined that they give similar results for bulk AlAs. Only local but not partial p theoretical DOS are available. Thus quantitative comparison can be reliably done on the position of peaks and not on their intensity.

Firstly, we consider the Al local DOS calculated for the $(GaAs)_1(AlAs)_1(100)$ system by the self-consistent FLAPW method (Figure 3(b)). Such a system represents a perfect interface. Its DOS is very similar to the sum of GaAs and AlAs DOS. Two changes are found with respect to the Al DOS of bulk AlAs: the slight shift in the main peak I and the presence of a supplementary peak on the high binding energy side of structure II, which corresponds to the Ga s states [2]. These two changes are present in our experimental results, the supplementary peak due to the mixing of Al 3p and Ga states being seen as a broadening of the structure at 5.7 eV towards the high binding energies. So we interpret

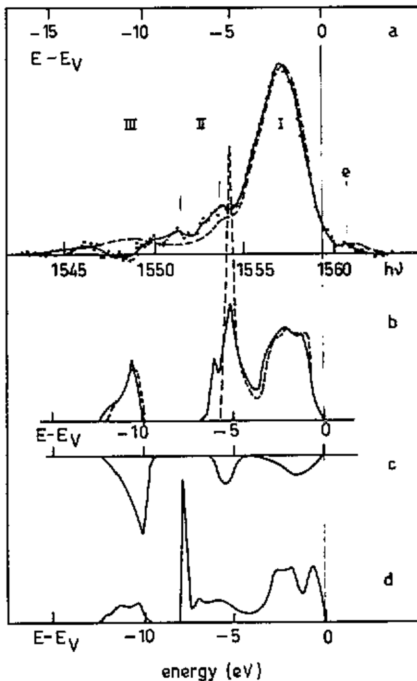

Figure 3. Valence states of AlAs on Al sites (a) Al 3p–1s emission from bulk AlAs (broken line) and GaAs–AlAs interface (experimental dots). Excitation feature is labelled e (see text). (b) Calculated local Al DOS of $(AlAs)_1(GaAs)_1$ (full line) compared with local As DOS of bulk AlAs (broken line) [2]. (c) Difference between the calculated DOS of AlAs at the Al site next to one As vacancy and the DOS of perfect AlAs [17]. (d) Calculated local Ga DOS of GaAs for a Ga–Ga wrong bond [18].

this first group of changes as due to the mixing of AlAs and GaAs valence states at the interface.

The disappearance of structure III reflects Al 3p and As 4s demixing and suggests the presence of As vacancies at the interface. The local Al DOS for AlAs with As vacancies has been calculated by using a one-electron tight binding scheme associated with a recursion method [17]; figure 3(c) shows the difference between the DOS calculated at the cation site next to one As vacancy and the DOS of perfect AlAs. A dip is present at about 10 eV in agreement with our experimental result. The two dips located towards the lower binding energies on figure 3(c) are in an energy range where the density of states is high and other changes are present; so, it is difficult to determine the effects due to this type of defect in this range.

When a lack of As exists, one expects the presence of cation–cation wrong bonds, i.e. of Al–Al, Ga–Ga or Al–Ga bonds. A tight binding recursion calculation shows that the presence of wrong bonds induces in the DOS of the III–V compounds a dominant structure with mainly s character at around 7 to 8 eV from E_v [18]. As an example, figure 3(d) shows the calculated local Ga DOS for a Ga–Ga wrong bond. The dominant structure is at 7.8 eV from E_v. Because the Al–Ga wrong bond is quite likely at the interface, the feature we observe at 7.8 eV from E_v in the Al DOS at the interface can be interpreted as due to the mixing of the valence states of Al and Ga in the vicinity of Ga–Al wrong

bonds at the interface. The presence of such wrong bonds indicates some imperfections of the AlAs surface on which is deposited the GaAs top layer.

3.2. *Excitation state*

An emission (labelled e on figure 3) is present towards the low binding energy of the peak I; its distance from the top of the valence band is 1.4 eV at the interface and 1.9 eV in the bulk; its intensity with respect to that of the main peak is of the order of 1% for both systems. By supposing that this emission is due to the deexcitation of a 1s core exciton and that its binding energy is the same at the interface and in the bulk, the gap in the interfacial zone should be $1.4 + 0.3 = 1.7$ eV. This value is intermediate between E_g for AlAs (2.2 eV) and GaAs (1.4 eV). One might suppose that, due to the roughness, E_g would vary continuously from 2.2 eV to 1.4 eV. Then the distance between E_v and the excitonic transition would vary from 1.9 to 1.1 eV; the transition would be broadened and difficult to observe. In contrast, feature e is narrower and better resolved at the interface than in the bulk, thus making the transition typical of the interface. From DOS calculated for the ideal $(GaAs)_1(AlAs)_1$ (100) interface, one expects E_g to be 1.9 eV, i.e. less than in the bulk. This value agrees with that assumed from our observations within the experimental accuracy.

On the other hand, in the presence of As vacancies, a strong peak is present in the calculated empty DOS at 1.5 eV above E_v. An excitonic-like state associated with this peak in the empty DOS could also be considered. In this case the decrease in the E_v–excitonic transition energy difference would confirm our interpretation made from the analysis of the valence states and would show that defects such as As vacancies would be present at the interface.

4. Conclusion

To conclude, the features corresponding to a strong mixing of Al 3p states with As states in bulk AlAs are far more modified at the interface than those corresponding to mainly Al 3p states. We have clearly found evidence for the mixing between valence states of AlAs and GaAs as expected for a perfect interface. The presence of point defects such as cation–cation wrong bonds and arsenic vacancies has clearly been observed for the samples studied here. Our results show the sensitivity of density of states measurements by EXES to determine the characteristics of deep interfacial zones.

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