

Ultraviolet photoelectron spectroscopy investigation of electron affinity and polarity on a cylindrical GaAs single crystal

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The orientation dependence of the electron affinity χ was measured by ultraviolet photoelectron spectroscopy on the surface of a cylindrically shaped GaAs crystal with $[1\bar{1}0]$ as its axis, prepared by ion bombardment without and with annealing as well as molecular-beam epitaxy. The polarity of GaAs and thus surface stoichiometry and relaxation give the main contribution to the variation of χ . Ga(As) turns out to be positively (negatively) charged. The results are consistent with a reduced charge on the surface atoms compared to the bulk.

Using synchrotron radiation it has become possible to measure the surface to bulk shift of the $3d$ core-level binding energies of Ga and As in GaAs.¹⁻³ Eastman *et al.*¹ have interpreted their data as mainly due to an initial-state effect indicating that the Ga (As) atoms at the relaxed (110) surface are more positively (negatively) charged than in the bulk. Assuming that the ionicity at the surface is reduced in comparison to the bulk this would indicate negatively charged Ga atoms in GaAs in contradiction to simple electronegativity arguments. Davenport *et al.*⁴ have reinterpreted the data of Eastman *et al.* and come to the conclusion that the changed surface Madelung potential gives an important contribution to the surface core-level shifts. They estimate the surface charges to be $\text{Ga}_s^{+0.28}\text{As}_s^{-0.28}$ which is of the sign expected from electronegativity and slightly lower than most of the estimated bulk values of $+0.3$ – $+0.4$ for Ga.^{5,6} However, also charges of opposite sign giving $\text{Ga}^{-0.39}$ were calculated.⁷ Measurements on (001) with different surface composition by Bachrach *et al.*² can directly be interpreted in terms of positive Ga and negative As atoms with reduced surface polarity. Very recently, Larsen *et al.*³ have measured an As $3d$ shift of $+0.62$ eV between bulk GaAs and a layer of amorphous As deposited on a GaAs(001)-(2×4) [or $c(2\times 8)$] surface. This shift is of the expected sign and a bulk charge of $\text{As}_b^{-0.3}$ is estimated. They find no shift between the bulk and the (2×4) surface atoms, however. For the Ga atoms this is understandable if the surface stoichiometry given by Larsen *et al.* is correct because then the surface consists of a full As layer. For the As $3d$ level, however, a zero shift would mean that the influence of a changed surface charge and the Madelung potential contribution (according to Davenport *et al.*) just cancel each other.

The following results on the orientation and preparation dependence of the electron affinity of GaAs clearly show that Ga (As) is positively (nega-

tively) charged at surface. They further yield arguments that the charge on surface atoms is appreciably lower than the bulk values, namely, approximately $\text{Ga}^{+0.1}\text{As}^{-0.1}$ when a bulk value of $\text{Ga}^{+0.33}\text{As}^{-0.33}$ is taken.

The sample was a Te-doped ($n \sim 6 \times 10^{17} \text{ cm}^{-3}$) ring-shaped n -type GaAs cylinder of 23 mm diam with $[1\bar{1}0]$ as its axis (for details see Ref. 8). Due to the relatively large beam diameter (~ 1 mm), the angle resolution was $\sim \pm 5^\circ$ in ultraviolet photoelectron spectroscopy (UPS). The sample was prepared in three different ways: (i) Ion bombardment (IB) with 2-kV ions, resulting in a completely disordered surface with Ga accumulation^{9,10} giving only a diffuse background in low-energy-electron diffraction (LEED). (ii) Ion bombardment and annealing (IBA) for 10 min at 500 °C, resulting in a well-ordered surface with clear LEED spots around and between (110) and (111). At (111) the well-known (2×2) structure,¹¹ and at (110) the (1×1) structure, appeared. Around (11 $\bar{2}$) also clear spots appeared indicating (110) facets. Around (001), (00 $\bar{1}$), and (11 $\bar{1}$), the LEED spots are weak with relatively high background indicating a high defect concentration. (iii) Molecular-beam epitaxy (MBE) on the IBA surface with one single evaporation cell containing GaAs.¹² At (001) and (00 $\bar{1}$) the As-rich $c(2\times 8)$ structure¹³ and at (11 $\bar{1}$) the As-rich (2×2) structure¹⁴ were prepared. At (111) and at (110) the structure was the same as after IBA with still slightly sharper spots. Between the low index orientations, stepped and/or faceted structures appeared as described elsewhere.¹⁵

The electron affinity χ is given by $\chi = h\nu - W - E_g$. W is the total width of the spectrum, corrected by an appropriate analyzer resolution term; $E_g = 1.35$ eV is the room-temperature energy-gap value. Both high- and low-energy edges of the spectra could be determined with a relative error of together ± 0.03 eV. The low-energy (secondary electron) cutoff is steep

and therefore easy to determine (see Fig. 1). The high-energy edge [valence-band (VB) edge], however, is not so sharp and its shape depends on the orientation- and preparation-dependent contribution from surface and defect states. Therefore the position of the He I excited Ga 3d emission peak was measured and its binding energy averaged over all orientations taken to be $-(18.8 \pm 0.2)$ eV below the VB edge. This represents the main contributions to the absolute error of χ which is estimated to be $\sim \pm 0.3$ eV.

UPS is a local probe of the surface potential. Thus, in certain cases, two values of the secondary threshold could be observed (Fig. 1), indicating that the surface contained two structurally different regions or domains. A relative measure of the concentration of these two domains can be taken from the slopes above the two thresholds.

For metals, it has been demonstrated both theoretically¹⁶ and experimentally^{17,18} that the work function ϕ is highest for closely packed surfaces and decreases due to the so-called charge "smoothing effect" as well for more open structure as for stepped surfaces where the decrease is proportional to the step concentration. For compounds, an additional ionic dipole contribution must be considered. For GaAs, especially the polar (11 $\bar{1}$) ("As-face") and (001) surfaces are of interest which should give a dipole contribution depending on the known preparation-dependent As content.¹³⁻¹⁵ Also on the nonpolar (110) surface, a dipole contribution is expected owing to the known

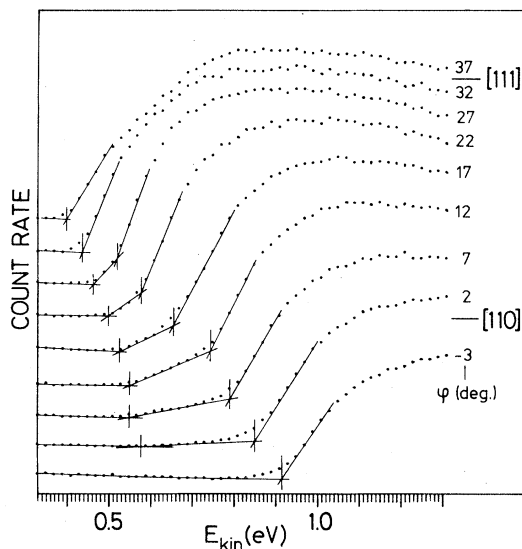


FIG. 1. Low-energy cutoff of He I excited spectra for the orientation range between [110] and [111]. Abscissa: E_{kin} with respect to the vacuum level of the analyzer. In this range appear two thresholds associated with two types of domains. The slope above the left-hand threshold is a relative measure of the population of the corresponding domains.

relaxation whose main feature is to tilt the As atoms of the first layer outward by $\sim 27^\circ$ and the As atoms of the second layer inward by $\sim -4.8^\circ$ with respect to the Ga atoms.¹⁹

Figure 2 shows the measured orientation dependence of χ . For the IB surface, χ is structureless and almost orientation independent. After IB, the surface layer is As depleted.^{9,10} So the low and almost constant value of χ is consistent with an accumulation of positively charged Ga at least in the topmost layer or even with a metallic Ga phase. That χ everywhere is lower than for the IBA and MBE surfaces is consistent with surface disorder which is expected to reduce χ .¹⁷

The orientation dependence of χ on the IBA surface is strong and consistent with $\text{Ga}^{+q}\text{As}^{-q}$. The value at (111), which is expected to be fully Ga terminated, is lowest; the value at (110) is high, consistent with a dipole contribution due to the relaxation as described above. At (11 $\bar{1}$) χ is higher than at (111), but lower than at (110) and (11 $\bar{2}$) which indicates partly but probably not complete As depletion [ideally (11 $\bar{1}$) would be As terminated], consistent with Auger results.¹⁴ Towards (11 $\bar{2}$), χ increases since there the surface consists mainly of (110) facets. At (001) and (00 $\bar{1}$), χ is comparably low which fits to the low As content on these surfaces after IBA.¹³ Between (111) and (110) two thresholds were found giving two χ values corresponding to two kinds of domains. The contribution of the one with lower χ decreases almost linearly from 100% at (111) to zero at (110) (see Fig. 1). It is attributed to larger (111) terraces, whereas the second threshold obviously is due to stepped regions with monatomic steps.¹⁵ The weak increase of χ on the terraces may be due to the increasing potential smearing along the edge of these terraces with decreasing width.

The MBE curve is identical to the IBA curve at (110) which confirms that both preparations give very similar surface compositions and structures. At

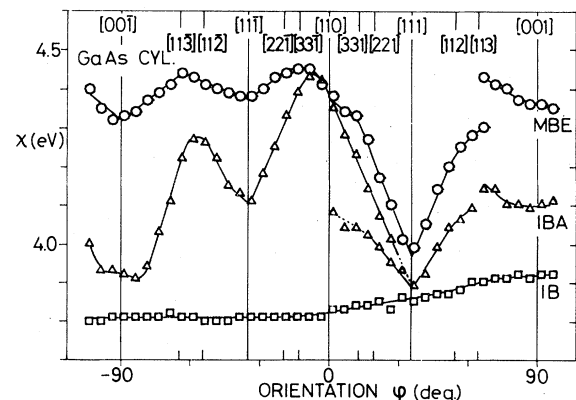


FIG. 2. Orientation dependence of the electron affinity χ for the surface prepared by MBE, IBA, and IB.

(111), χ is somewhat higher than for IBA which probably is due to a reduced defect concentration for MBE. Both on (11 $\bar{1}$) and (00 $\bar{1}$), (001), χ is strongly increased upon MBE which is due to the increased As content of the surface layer.

The decrease from (110) towards (111) is less steep at first, which is consistent with the formation of two-atomic $n(110) \times 2(111)$ steps upon MBE (Ref. 15) and correspondingly a reduced edge site concentration. That the slope of χ is reduced by more than a factor of $\frac{1}{2}$ agrees with an energetically more favorable relaxation at double-layer steps for which qualitative arguments have been given.^{8,20} Later, the slope corresponds to $1(110) \times n(111)$ steps as on the IBA surface.

An important detail is that the maximum of χ is not at (110) but that χ increases further towards (11 $\bar{1}$) with a slope corresponding to the $n(110) \times 1(111)$ single steps of the IBA surface. Both IBA and MBE curves coincide at first, which is consistent with the same step structure of $n(110) \times 1(11\bar{1})$ steps for both preparations as proved by LEED at $\sim 10^\circ$ off (110) towards (11 $\bar{1}$). This behavior again is understandable in terms of the ionic character with Ga being positively charged and the prevalence of the ionicity influence on the variation of χ . When going from (110) towards (111), the atoms at the edge are Ga atoms and the step riser consists of (111) Ga sites. This reduces χ because of the positive charge on Ga. Going towards (11 $\bar{1}$), the edge and riser atoms are negatively charged As atoms. That the IBA curve continues linearly across (110) is a hint that the usual charge smoothing contribution to the variation of χ is small compared to the ionicity contribution. The increase of χ from (110) towards (11 $\bar{1}$) stops when (11 $\bar{1}$) terraces begin to become dominant so that χ decreases from IBA because of As depletion and begins to be dominated by the (11 $\bar{1}$) relaxation mechanism for MBE.

According to the Helmholtz equation,¹⁷

$$\Delta\chi = 300 \times 10^{18} 4\pi n \mu, \quad (1)$$

the electron affinity change $\Delta\chi$ in eV is related to the

number n in cm^{-2} of dipoles with the dipole moment μ in Debye units D. For the orientations where the step height and the concentration is known,¹⁵ Table I gives the corresponding dipole moments. The absolute values of the dipole moments are comparable with those found for metals.^{17,18} However, the sign is opposite for most cases, which means that χ increases with increasing step density which again demonstrates the dominant influence of ionicity.

From μ the charge $\pm q$ related with the surface Ga and As atoms can be calculated, provided the surface composition and geometry are known. For the (111) surface, a complete first Ga layer seems reasonable and is consistent with its easy and reproducible preparation. For the (11 $\bar{1}$)- 2×2 surface prepared by MBE, a surface As concentration of 0.87 has been measured¹⁴ and arguments were given that an ideal value of 1 is probable.²¹ Under the assumption of complete surface layers without strong relaxation, the difference $\Delta\chi_{(111)-(11\bar{1})}$ between (111) and (11 $\bar{1}$), which is 0.4 eV for the MBE surface, would give a surface charge corresponding to $\text{Ga}_s^{+0.038}\text{As}_s^{-0.038}$.

From electrostatic reasons the charge contained in the topmost layers of (111) and (11 $\bar{1}$) must be reduced by $\frac{1}{4}$ of the corresponding bulk layer value.²²

Thus the bulk values derived from the surface charge would be $\text{Ga}_b^{+0.051}\text{As}_b^{-0.051}$. These values are considerably lower than most estimates.^{5,6} The most probable reason is that the surface dipole contribution is reduced by the surface relaxation mechanism about which only few details are known. It is, however, consistent with results from angle resolved UPS on the dangling bond states on the (11 $\bar{1}$)- 2×2 surface,²¹ which were found to be essentially *s*-like. This corresponds to a less ionic surface As. Also on (111)Ga, a tendency of the surface Ga layer towards a metallic (neutral) configuration is plausible. Actually such a charge compensation mechanism is necessary since a charge value of ± 0.33 to ± 0.38 , as has been estimated for the bulk,^{3,6} would induce a $\Delta\chi_{(111)-(11\bar{1})}$ of 3.5 to 4.0 eV for the ideal surfaces which is highly unreasonable because of energetic reasons.

Another estimation of the surface ionicity is possi-

TABLE I. Dipole moment μ per edge site in Debye units for the regions where the surfaces are stepped and the step height is known from LEED. Positive sign: χ decreases with increasing step concentration.

Step configuration	Nearest low index orientation	μ after preparation	
		IBA	MBE
$n(110) \times 1(11\bar{1})$	(110)	-0.16 ± 0.03	-0.16 ± 0.03
$n(110) \times 1(111)$	(110)	$+0.16 \pm 0.02$	
$n(110) \times 2(111)$	(110)		$+0.10 \pm 0.03$
$n(111) \times 1(110)$	(111)	-0.28 ± 0.04	-0.30 ± 0.04
$n(111) \times 1(001)$	(111)	-0.20 ± 0.03	-0.32 ± 0.03

ble when the (111)- 2×2 Ga and the (11 $\bar{1}$)- 2×2 As surfaces are assumed to yield an ionic contribution to χ which has the same magnitude but is opposite in sign. Then the unrelaxed (110) surface should have a χ halfway between the values for (111) and (11 $\bar{1}$). Experimentally χ is found 0.20 eV higher which is due to the relaxation induced dipole contribution. The relaxation of the second layer is opposite to the first one (tilt angle $\omega_2 = -4.8^\circ$, As inward¹⁹) and partly cancels the first-layer dipole contribution ($\omega_1 = 27.3^\circ$, As outward¹⁹). When a bulk charge value of ± 0.33 (Ref. 3) is assumed for the second layer, the Helmholtz Eq. (1) yields a first-layer dipole corresponding to $\text{Ga}_s^{+0.10}\text{As}_s^{-0.10}$. Again the surface charge is found to be smaller than the bulk charge.

In conclusion, it has been shown that the orienta-

tion dependence of χ on GaAs can be explained only with the polarity $\text{Ga}^+q\text{As}^{-q}$. The results strongly support a surface polarity reduced in comparison to the bulk with $q_s \sim 0.04$ to 0.10. The charge smoothing contribution to $\Delta\chi$ is less important than the polarity contribution.

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