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High-resolution synchrotron-radiation core-level spectroscopy of decapped GaAs(100) surfaces

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We report a high-resolution core-level spectroscopy study of the (4×2)-$c(8\times2)$ GaAs(100) surface prepared by thermal decapping of surfaces grown by molecular-beam epitaxy. Ga and As $3d$ core levels are analyzed using very strict parameter conditions, and compared with core levels taken from cleaved GaAs(110). Two surface components are resolved in the Ga spectra while only one surface component is necessary for As. We tentatively assign the two Ga surface components to inequivalent Ga dimers in the unit cell; the As surface component is assigned to the threefold-coordinated second-layer As next to the missing row of Ga dimers. The position of the Fermi level on decapped n-type and p-type substrates is investigated in detail. The characterization of these clean decapped (100) surfaces provides a firm basis for further studies of electrical and chemical properties of metal-semiconductor interfaces.

I. INTRODUCTION

Recent studies of the formation of metal-semiconductor interfaces have focused on GaAs substrates grown by molecular-beam epitaxy (MBE) and protected by a thick As layer for ambient transfer.[1-4] A natural evolution of Schottky-barrier work toward technologically relevant surfaces means that As-capped surfaces will be extensively used in years to come. A detailed understanding of their structure, chemical composition, and electronic properties upon thermal decapping is therefore essential. The most recent structural work is a scanning-tunneling-microscopy investigation of the As-rich (2×4)-$c(2\times8)$ GaAs(100) reconstruction obtained after decapping at 450 °C.[5] The model is based on a regular array of missing As dimers, in agreement with predictions from total-energy calculations.[6] The position of the Fermi level (E_F) on freshly decapped surfaces has been measured[1-4] and there is general agreement on the fact that the initial equilibrium position is around 0.5 eV and 0.7 eV above the valence-band maximum (VBM) on p-type GaAs and n-type GaAs, respectively. Yet, the difficulty of accurately controlling surface temperature and As desorption leads to some uncertainty on the composition of these decapped surfaces. The relation between surface electronic properties and atomic structure and composition thus remains undefined.

It is important to establish a common ground to evaluate composition versus structure on these decapped surfaces. We present here a high-resolution core-level spectroscopy study of the Ga-rich surface used in recent studies of Schottky-barrier formation.[1-4] We correlate this work with observations of surface reconstructions with low-energy electron diffraction (LEED). We use the cleaved (110) GaAs surface as a reference for the adjustment of the core-level deconvolution parameters. We provide a detailed deconvolution of the Ga and As $3d$ core levels which serves as a basis for the analysis of the formation of metal-GaAs(100) interfaces.[7]

II. EXPERIMENT

Highly doped n-type (Si, $\geq 10^{18}$ cm^{-3}) and p-type (Be, $\geq 10^{18}$ cm^{-3}) (100) GaAs layers, grown and As capped in two different MBE machines, were studied on the Mark V grasshopper monochromator beam line at the Synchrotron Radiation Center of the University of Wisconsin. The base pressure in the analysis chamber was $\sim 8\times10^{-11}$ torr. Photoemitted electrons were collected in an angle-integrated mode with a double-pass cylindrical mirror analyzer. For the energy range used in this work, the combined resolution of the monochromator and analyzer was better than 0.25 eV as measured from the Fermi edge of a thick Au film evaporated *in situ*.

As decapping was done in several steps. The bulk of the As layer was removed at 350 °C and the annealing was stopped to allow the pressure to recover. The final decapping was done by successive annealing cycles of a few seconds at temperatures up to 570 °C. The temperature

was measured with an infrared pyrometer aiming at the sample through a sapphire window. The measurement was precalibrated with a thermocouple in contact with the GaAs surface. In a separate LEED experiment, decapping at various temperatures produced the expected range of structures from the As-rich (2×4)-$c(2\times8)$ reconstruction around 450 °C to the Ga-rich (4×2)-$c(8\times2)$ reconstruction at 570 °C. Finally, the (110) surfaces were produced by *in situ* cleaving *n*-type (Si, 10^{17} cm^{-3}) GaAs bars.

III. RESULTS AND DISCUSSION

Core-level deconvolution is very powerful, provided that it is performed in a very consistent fashion. We followed the guide lines outlined by Joyce, Del Giudice, and Weaver,[8] placed very stringent conditions on all parameters involved and used a minimum number of components in the fit. In this paper, the energy position of the surface core-level components are referenced to the bulk component with a "+" or "−" sign, indicating a shift toward higher or lower binding energy (BE), respectively.

We compare the Ga 3*d* and As 3*d* core levels measured on the (110) and (100) surfaces with 100-eV photons. This energy provides maximum surface sensitivity with nearly identical escape depths for the photoemitted Ga and As 3*d* electrons. Figure 1 shows the result of the deconvolution with simultaneous subtraction of an integrated background[8] for the (110) surface. As expected from the surface relaxation,[9] single Ga and As surface components are sufficient to produce an excellent fit of the data. This was originally shown by Eastman *et al.*[10] The deconvolution parameters are given in Table I. The fixed parameters are the spin-orbit splitting and the Lorentzian widths (core-hole lifetime). Also fixed but not shown in Table I is the energy separation between the $3d_{5/2}$ Ga and As bulk components ($\Delta E = 21.85$ eV) determined from spectra acquired in a bulk-sensitive mode. The Ga and As Lorentzian widths are fully consistent with the Lorentzian

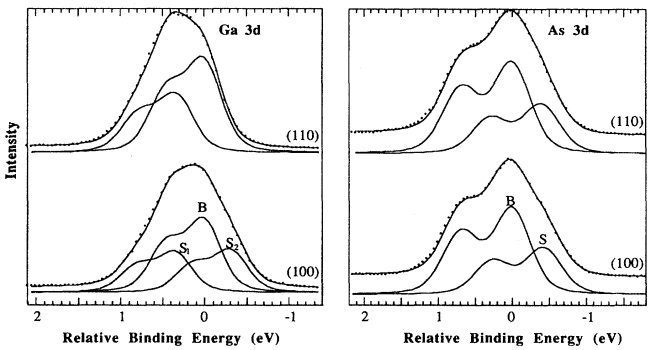

FIG. 1. Deconvolution of the Ga 3*d* and As 3*d* photoemission spectra measured from GaAs(110) and (100) surfaces. The photon energy is 100 eV. The solid line through the data points is the result of the fit. The deconvolution parameters are given in Table I.

TABLE I. Fitting parameters for the Ga 3*d* and As 3*d* core-level spectra for the clean GaAs(100) and (110) surfaces. All energies are in eV.

	Ga 3*d*	As 3*d*
Spin-orbit splitting	0.45	0.69
Branching ratio	1.50	1.40
Gaussian width	0.39	0.48
Lorentzian width	0.155	0.17
BE shift of S_1 (100)	0.34	−0.43
BE shift of S_2 (100)	−0.32	
BE shift of S (110)	0.33	−0.40

width used in recent high-resolution work on Ge (0.15 eV)[11] and with the values obtained by Miller and Chiang.[12] The branching ratios for Ga and As are allowed to vary by a maximum of 7% around the statistical value of 1.5. We also impose the same shape for the bulk and surface components. Excellent fits for Si 2*p* and Ge 3*d* core levels for different surface reconstructions can be achieved with Gaussian widths identical for bulk and surface components and equal to the experimental resolution[11] because phonon coupling is weak for elemental crystals.[13] For room-temperature GaAs, however, phonon broadening increases the full width at half maximum (FWHM) to 0.39 and 0.48 eV for Ga and As, respectively, considerably larger than the 0.25-eV experimental resolution.

The two-step decapping procedure (350 and 570 °C) for the (100) surface produces a Ga-rich composition, as indicated by the (4×2)-$c(8\times2)$ LEED pattern.[14] We use the same fitting parameters as those used in the deconvolution of the (110) core levels. In this case, however, two surface components, S_1 and S_2 on either side of the bulk component *B*, are necessary to achieve a good fit of the Ga core level (Fig. 1). This is clearly not an artifact of the deconvolution, as indicated by the marked difference between the shape of the Ga 3*d* spectrum of the (100) and (110) surfaces. For As, on the other hand, a single surface component is sufficient to provide an excellent fit. The shifts of all these components with respect to the bulk components are given in Table I.

The S_1 and S_2 Ga components reveal the presence of inequivalent surface Ga sites in the (4×2) unit cell. We assume here that the (4×2)-$c(8\times2)$ Ga-rich reconstruction is explained by a missing Ga dimer row model. Asymmetric dimers could provide an explanation for the two surface Ga components, although they are not presently favored by theoretical calculations.[6] There are, however, inequivalent dimers in the cell: one type-1 dimer, in which Ga is bonded to fourfold-coordinated second-layer As, surrounded by two type-2 dimers, in which Ga is bonded to threefold-coordinated second-layer As, next to the missing dimer row. The fourfold-coordinated second-layer As are basically equivalent to bulk As (*B* component), whereas the threefold-coordinated As is likely to get in a p^3-like configuration similar to that found on the (110) surface.[15] We propose therefore that the threefold-coordinated As produce the *S* component which is found at the same BE as the (110)

surface. Similarly, we associate the S_1 and S_2 Ga components with the two inequivalent dimers. A specific assignment is still uncertain, although preliminary calculations indicate that Ga in type-1 dimers have a sizable fraction ($\sim$0.2) of an electron less than Ga in type-2 dimers.[15] S_1 and S_2 components could therefore be tentatively assigned to type-1 and type-2 dimers, respectively.

We also performed progressive decapping through short temperature cycles between 350 °C and temperatures above the decomposition temperature of the surface ($\sim$650 °C). The results are shown in Fig. 2. At the lowest temperature, excess elemental As is seen as a broad component (FWHM =0.6 eV) shifted by +0.6 eV with respect to the bulk component [panel (a)]. It attenuates at intermediate temperature [panel (b)] where the As-rich (2×4)-c(2×8) structure is seen. This result is in good agreement with earlier studies done on MBE-grown surfaces.[16] In that work, the low BE S component was associated with the atoms terminating the polar surface, presumably the As dimers. It is likely, however, that part of the high BE component is also due to inequivalent As dimers, much as was discussed above for the Ga dimers of the (4×2) structure. In the same temperature range, Ga already exhibits two surface components [panels (a) and (b)] which were not seen on the MBE-grown surfaces.[16,17] At the temperature where the (4×2)-c(8×2) Ga-rich reconstruction is formed ($\sim$550 °C), all excess As (high BE component) and As dimers desorb [panel (c)], and the relative weight of the S_1 and S_2 surface Ga components reverses. Above the surface decomposition temperature, an additional Ga component [panel (d)] at −0.9 eV indicates a loss of As from the surface and formation of metallic Ga clusters. This is accompanied by the formation of (110) facets clearly seen in the LEED pattern. The best fit of this metallic Ga component is obtained with a Doniach-Sunjic line shape with an asymmetry parameter of 0.08.[18] Interestingly, the FWHM of this component is equal to the total instrumental resolution (0.25 eV), whereas the substrate surface and bulk Ga components still require a 0.39-eV FWHM. In addition, the intensity of the S_1 component is markedly enhanced. Its ratio to the bulk component approaches that of the cleaved (110) surface, consistent with the formation of (110) facets. At these temperatures, however, LEED shows that parts of the surface retain the (100) orientation with the (4×2)-c(8×2) reconstruction, and the S_2 Ga component persists in the deconvolution [panel (d)]. This is a clear indication that this component is indeed associated with Ga dimers, the building blocks of the (4×2)-c(8×2) reconstruction.

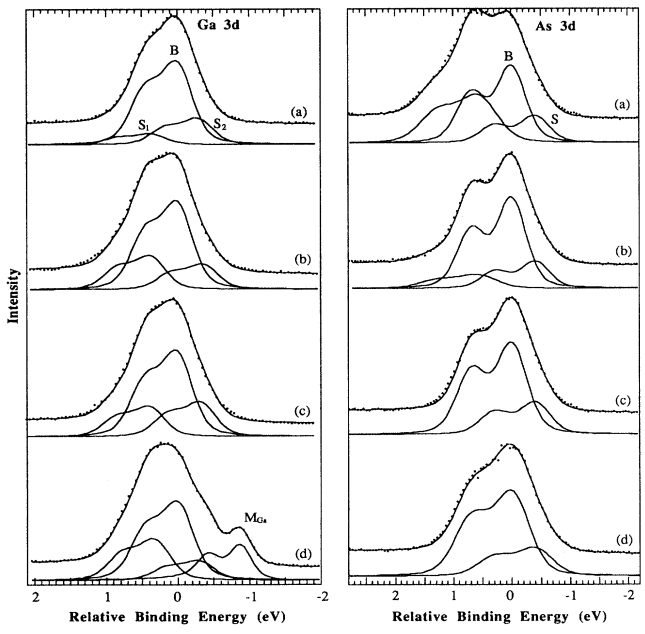

FIG. 2. Deconvolution of the Ga 3d and As 3d photoemission spectra measured from the GaAs(100) surface decapped at increasingly higher temperatures [from panel (a) to panel (d)]. The photon energy is 100 eV for As and 80 eV for Ga.

Photoemission measurements on more than ten samples show that the positions of E_F on both n- and p-type decapped surfaces are centered around 0.70 ± 0.05 and 0.55 ± 0.05 eV above the VBM, respectively, in agreement with previous work.[2,19] These values were determined from the position of the VBM with respect to E_F (usual linear approximation) as well as from a comparison with the core-level positions on well-cleaved (110) surfaces. They are subject to a maximum uncertainty of 0.05 eV. We verified with a Kelvin probe[4] that these measurements were not affected by surface photovoltage under our experimental conditions (doping $> 10^{18}$ cm^{-8}, room temperature and photon flux $\sim 10^{10}$/scm^2). We can therefore ascertain that the difference between the n- and p-type E_F positions is a genuine result of the density and type of the initial surface states in the semiconductor gap. The remarkable point is that, within the range of uncertainty quoted above, the position of E_F does not change with decapping temperature and, therefore, not with the surface composition. The position of E_F on n-type samples coincides with the position found on MBE-grown c(2×8) surfaces.[20] In the decapping temperature regime leading to Ga-rich surfaces, however, we do not find the 0.2-eV drop of E_F toward the VBM reported for the MBE (4×6) surface.[20]

The initial position of E_F leads to the conclusion that both acceptor and donorlike surface states are present deep in the gap of the decapped surfaces. Their density appears to be fairly low, however. We have shown, for example, that the adsorption of 10^{-2} monolayer of In ($\sim 6 \times 10^{12}$ cm^{-2}) is sufficient to move E_F up by 50 meV from its initial position of 0.7 eV above VBM on n-type GaAs.[4] At these low coverages, In is adsorbed as isolated adatoms and does not have a significant long-range effect on the GaAs surface reconstruction. These initial surface states cannot therefore be associated with the building blocks of the structure, i.e., the dimers, which have a much higher density (5×10^{14} cm^{-2}). As a matter of fact, calculations for the (2×1) structure, i.e., no missing dimer row, show that no surface state deep in the gap should be associated with these dimers.[21] The states responsible for the initial bending are more likely the result of residual surface defects or incomplete removal of the protective As layer.

IV. SUMMARY

We have analyzed high-resolution Ga and As 3*d* core-level spectra measured from decapped MBE-grown GaAs(100) surfaces. A comparison with data from cleaved (110) surfaces shows significant differences in the Ga 3*d* line shape which have to be accounted for by two surface components on either side of the bulk line. These are tentatively associated with inequivalent Ga dimers of the (4×2)-$c(8\times2)$ unit cell. The Fermi level is consistently found at 0.7 and 0.55 eV above the valence-band maximum on *n*- and *p*-type samples, regardless of the surface As composition.

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