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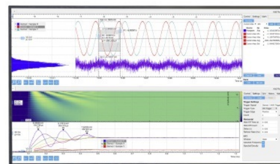

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Valence band discontinuity at a cubic GaN/GaAs heterojunction measured by synchrotron-radiation photoemission spectroscopy

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The valence band discontinuity of the n-type cubic GaN/GaAs heterojunction is measured by means of angle-resolved photoemission spectroscopy using synchrotron radiation. High quality cubic GaN films are grown on GaAs(100) substrates by nitrogen plasma-assisted molecular beam epitaxy, and the valence band discontinuity is determined by a combination of core and valence level spectra. A value of $\Delta E_V=(1.84\pm0.1)$ eV across the GaN/GaAs heterojunction is obtained, which means that the discontinuity in the conduction bands at this interface is very small, such that a vertical contact scheme may be realized for GaN/GaAs heterojunctions. © *1997 American Institute of Physics.*
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Gallium nitride has attracted considerable interest in view of its use for optoelectronic devices in the blue-green spectral region. Currently, research focuses on heterojunction device applications based on GaN and its alloys, following improvements in material quality.[1] Thus, an investigation on the band offset at heterojunctions of nitrides and other materials is important for device design, modeling, and performance prediction. The valence band discontinuity at the wurtzite AlN/GaN interface has been measured by x-ray photoemission spectroscopy.[2,3] Recently, Yang *et al.*[4] have demonstrated that cubic GaN films can been grown on GaAs (100), with a sharp interface between the epitaxial layer and the substrate. This makes it possible to determine the band offset at the GaN/GaAs heterojunction, which is interesting also because a large conduction band offset might hinder charge transport across this interface, thus prohibiting the highly desirable vertical contact scheme for light-emitting devices on n-GaAs. This letter presents the first report of a measurement of the valence band discontinuity at the cubic GaN(100)/GaAs(100) interface, using angle-resolved synchrotron radiation photoemission spectroscopy.

Cubic n-type GaN(100) samples with three nominal thicknesses (1000, 50, and 18 Å) were grown by plasma-assisted molecular beam epitaxy (MBE) on n-type GaAs(100) substrates in a separate chamber.[4,5] They were loaded into the UHV ($\sim1\times10^{-10}$ mbar) analysis chamber, equipped with an angle-resolved photoelectron spectrometer (ADES 400, VG Scientific, UK), low energy electron diffraction (LEED) optics, and sample heating and cooling facilities, after transfer through air, and a brief etch in HCl. Photoelectrons were excited by light from the BESSY storage ring and dispersed by the toroidal grating monochromators TGM4 and TGM6; the overall resolution as measured from the width of the Fermi edge of a clean gold specimen in contact with the samples was 150 meV. Additional experiments were carried out in a conventional x-ray photoelectron spectrometer using Mg $K\alpha$ (1256.3 eV) photons. Clean surfaces were prepared by annealing to 600–650 °C. (1×1) LEED patterns and clear signatures of band-to-band transitions were observed, such as reported in a recent study of the band structure of cubic GaN.[6] The details of the experimental technique and sample preparation may be found elsewhere.[6]

X-ray photoemission spectroscopy, and photoemission with synchrotron radiation in particular have been extensively used to measure the valence-band discontinuity ΔE_V at a heterojunction interface. The method of measurement and calculation has been described in the literature.[7] The inset of Fig. 1 shows the sample structure. The valence-band

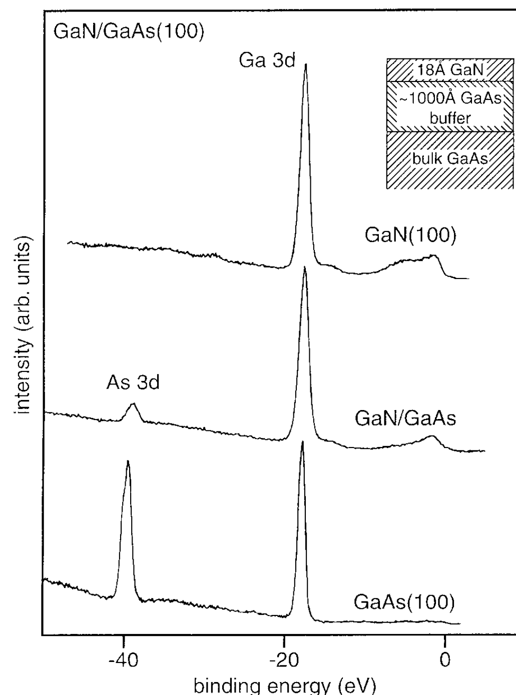

FIG. 1. Core and valence level spectra of clean GaAs(100), an 18 Å layer of cubic GaN on GaAs(100), and a thick layer of GaN(100), recorded in normal emission using a photon energy of 90 eV. The inset shows the structure of the layer from which the center spectrum was recorded.

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discontinuity at the GaN/GaAs interface can be evaluated from the energy separation between the As $3d$ and Ga $3d$ core levels and the valence-band maximum (VBM) by

$$\Delta E_V = (E_V - \text{As } 3d)^{\text{GaAs}} - (E_V - \text{Ga } 3d)^{\text{GaN}} - \Delta E_{\text{cl}}(\text{Ga } 3d^{\text{GaN}} - \text{As } 3d^{\text{GaAs}}), \quad (1)$$

where $(E_V - \text{As } 3d)^{\text{GaAs}}$ is the binding energy of the As $3d$ peak in bulk GaAs, and $(E_V - \text{Ga } 3d)^{\text{GaN}}$ is the binding energy of the Ga $3d$ peak in bulk GaN, both with respect to the VBM. $\Delta E_{\text{cl}}(\text{Ga } 3d^{\text{GaN}} - \text{As } 3d^{\text{GaAs}})$ is the energy difference between the As $3d$ and Ga $3d$ from a heterojunction between the two semiconductors, in which the top the GaN layer is just thin enough to permit detection of the As $3d$ core levels from the GaAs substrate. These considerations only apply in a junction where the lattice mismatch does not introduce a strain in the overlayer which causes the core level binding energies to deviate from the values measured for an (unstrained) bulk sample, as shown for the Si/Ge heterojunction,[8,9] for example. The situation for GaN/GaAs is discussed below.

A clean GaAs(100) surface was prepared by annealing a piece of n-type ''epiready'' GaAs(100) sample (MCP Ltd, UK) at about 600 °C under an As overpressure of 10^{-8} mbar in order to obtain a reference for $(E_V - \text{As } 3d)^{\text{GaAs}}$. Le Lay *et al.*[10] have reported the energy separation between the Ga $3d_{5/2}$ and As bulk component as 21.85 eV from a clean decapped GaAs(100) surface using high-resolution synchrotron-radiation core-level spectroscopy, very close to our result of 21.88 eV. Measurements from a bulklike n-type GaN(100) film grown on GaAs(100) substrate with a thickness of about 1000 Å were used to determine the energy separation between the Ga $3d$ peak and the VBM for clean GaN. For the simultaneous measurement of Ga overlayer and As substrate core levels, heterojunctions were fabricated as thin (~18 and 50 Å) overlayers of GaN grown on GaAs(100) in order to detect the As $3d$ electrons emission from the substrate. In Fig. 1, overview spectra from these samples recorded in normal emission are shown, including the As $3d$, Ga $3d$ core levels, and valence band. The core-level position is defined as the half-width point at half-height and can be determined to within 0.02 eV by fitting a Gaussian/Lorentzian curve to the measured peak. From the intensity of the As $3d$ peak and the known electron mean free paths, it appears that the GaN overlayer may be somewhat thinner than the nominal thickness determined from the MBE growth process; assuming an electron mean free path of 5 Å, the spectrum of Fig. 1 would correspond to about 12 Å. This could be due to a thinning of the overlayer in the chemical etch/annealing process where a certain quantity of the overlayer may be lost due to desorption of the oxide formed during transport in air, or due to intermixing at the interface; if this were to amount to only two layers of GaN, it would explain the observed discrepancy.

The VBM is more difficult to locate. VBM spectra from the bulk GaAs and GaN surfaces were recorded and are shown in Fig. 2, where the VBM positions were determined by a linear extrapolation of the leading edge of the valence band spectra. The accuracy of our determination of ΔE_V is primarily limited by the determination of the valence band edge from the experimental spectra. Repeated tests on a large number of measurements indicate that ±0.05 eV is the typical accuracy in determining the VBM with this approach. The corresponding accuracy of our measurements is ±0.07 eV for ΔE_V. Note that, unlike in other heterojunctions, the valence band offset cannot be directly inferred from the two structures in the VBM spectrum of the GaN/GaAs junction (center spectrum of Fig. 2), since GaN exhibits considerable gap emission above the VBM as seen in the top spectrum (see also Ref. 6). The valence-band maximum is used as reference, and the binding energies of Ga $3d$ and As $3d$ peaks from bulk GaAs(100) and cubic GaN(100) surfaces relative to their reference energies are 17.66±0.07 and 40.80 ±0.07 eV, respectively. The core-level binding energy difference across the interface, ΔE_{cl}(Ga–As), has been measured independently many times, and its average value is 21.30±0.03 eV. Since the GaN/GaAs heterojunction has a 20% lattice mismatch, the effect of strain must be considered. For such a large mismatch, the critical thickness for the relaxation of the strained layer by the creation of dislocation is less than one monolayer,[11] such that the growing GaN overlayer will be unstrained from the outset. A large body of results, in particular high resolution transmission electron microscopy data,[12] demonstrates that even thin layers of GaN on GaAs are perfectly relaxed, such that strain effectively does not play a role in the investigation of the band offset. Epitaxial growth at this extreme mismatch (20%) is shown to arise, by a combination of reflection high-energy electron diffraction (RHEED) and TEM studies, from a coincidence lattice between GaAs and GaN. The mismatch between GaN and GaAs is seen to be relieved by Lomer dislocations formed every 5 interatomic distances, and this regular spacing is observed along both [110] directions. This coincidence leads to causes the *residual* misfit $f = (na_{\text{GaN}} - ma_{\text{GaAs}})/ma_{\text{GaAs}}$ to be only -0.02% for $n=5$ and $m=4$,

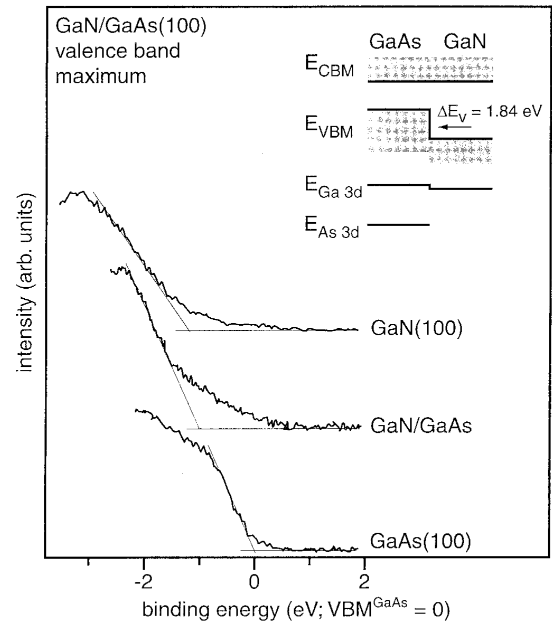

FIG. 2. Spectra in the valence band maximum region of clean GaAs(100), and 18 Å layer of cubic GaN on GaAs(100), and a thick cubic GaN(100) layer. The inset shows the band arrangement at the GaN/GaAs interface derived from a combined analysis of data in Figs. 1 and 2.

such that the array of Lomer dislocations will account for the entire misfit.[12] Also, RHEED line scans in layers of 5 monolayers upwards yield an identical in-plane lattice constant of 4.53 Å.[13] Further, x-ray diffraction have shown the absence of tetragonal distortion even at the lowest layer thicknesses.[13] Local strain arising from stacking faults and dislocations will exist, such that the band gap and all electronic levels will exhibit local variations, but these will only lead to a broadening of all levels.

The valence band discontinuity, ΔE_V, at the GaN/GaAs interface is thus calculated in a straightforward manner using Eq. (1) as $\Delta E_V = 40.80 - 17.66 - 21.30 = (1.84 \pm 0.1)$ eV. Since the 18 Å layer used in the synchrotron radiation experiments is rather thin, additional experiments were carried out on a 50 Å sample using x-ray photoelectron spectroscopy (XPS, $h\nu = 1253.6$ eV) where the Ga 3d and As 3d photoelectrons have a much larger escape depth, with an overall resolution of about 0.9 eV. This gave a slightly lower band offset ($\Delta E_V = 1.74$ eV), though still within the experimental error. The difference can be traced to a shift of the Ga 3d peak induced by the contribution of the substrate at slightly higher kinetic energies. The XPS experiment also served to exclude the possible influence of traces of arsenic incorporated into the GaN layer during growth, which were found to diffuse to the surface during annealing.

Taking the band gap of GaAs and GaN at room temperature as 1.42 (Ref. 13) and 3.23 eV,[14] respectively, the conduction band discontinuity of the GaN/GaAs heterojunction is estimated to be quite small, only about -0.03 eV. Due to the scatter in the determination of the band gap of cubic GaN, which amounts to about ± 0.1 eV, and our experimental error, a determination of the heterojunction type (staggered or straddling) is not possible at present, but the barrier to charge transport in the conduction band would be small in any case. The relative alignment of the valence and conduction bands is shown in the inset of Fig. 2. As for the magnitude of the valence band offset, to our knowledge no theoretical calculation of the valence band discontinuity at the GaN/GaAs heterojunction has been published. This would in any case be difficult within supercell calculations in a system with a lattice mismatch of 20%. Thus, we rely on the dielectric midgap energy (DME) model of Cardona and Christensen[15,16] to estimate the band offset between two semiconductors from their bulk structures and dielectric constants. The DME for GaAs has been tabulated by these authors.[16] Mönch[17] has recently calculated this parameter for cubic GaN on the basis of the empirical tight binding method, and has obtained a value of 2.25 eV above the VBM. Taken together with the value for GaAs, he obtains a valence band discontinuity of $\Delta E_V^{\mathrm{DME}} = 1.85$ eV, which agrees very closely with our experimental value. Comparing the deep levels of iron in GaN (Ref. 18) and GaAs, Fazzio[19] has estimated the valence band discontinuity as 2.04 eV, which is in fair agreement with the experimental value, given the errors of calculation and measurement. Our investigations thus indicate that a vertical contact scheme may be realized in the GaN/GaAs heterojunction.

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