

Strain dependence of the valence-band offset in InAs/GaAs heterojunctions determined by ultraviolet photoelectron spectroscopy

C. Ohler, R. Kohleick, A. Förster, and H. Lüth

Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich G.m.b.H., D-52425 Jülich, Germany

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We have used ultraviolet photoelectron spectroscopy to study the strain dependence of the valence-band offset *in situ* for InAs/GaAs(100) heterojunctions grown by molecular-beam epitaxy. The Ga $3d_{5/2}$ and In $4d_{5/2}$ core-level to valence-band-maximum binding-energy separations and the Ga $3d_{5/2}$ to In $4d_{5/2}$ core-level energy separations were measured as functions of strain. This requires the growth of fully relaxed $\text{In}_x\text{Ga}_{1-x}\text{As}$ buffer layers of varying composition as virtual substrates. We account for the true shape of the density of states near the valence-band edge by using results of $\mathbf{k} \cdot \mathbf{p}$ theory. Thus a full empirical pseudopotential calculation can be avoided. Our measurements yield valence-band offset values of 0.04 ± 0.10 eV for InAs strained to GaAs(100), 0.57 ± 0.10 eV for GaAs strained to InAs, and 0.36 ± 0.06 eV for both strained to InP(100), respectively, the valence-band maximum being *lower* at the InAs side of the junction.

I. INTRODUCTION

Some scientific effort has been devoted to the question as to what determines the band lineup at semiconductor heterojunctions. Due to possible applications of strained layers in high-speed and optoelectronic devices¹ and the increasing quality of pseudomorphic growth, recent experimental and theoretical work considered materials with different lattice constants and the dependence of band offsets on the strain condition imposed by different substrates. In addition, it has been judged possible² that the determination of the strain dependence of band offsets could shed light upon the virtue of different model theories, since all proposed reference levels are, in principle, functions of the band structure and hence of strain. The use of photoelectron spectroscopy to measure valence-band offsets of lattice matched materials is well established and has been extended to mismatched junctions.³

The InAs/GaAs system exhibiting a lattice mismatch of 7% is of some interest in the optoelectronic industry, and it is the most simple mismatched system of III-V semiconductors; its behavior may serve as a guideline for other compound semiconductor heterojunctions. Various theoretical investigations, both model theories and *ab initio* calculations, predict a large strain-induced variation of the band offset.⁴⁻⁷ No comprehensive experimental investigation of the subject has been carried out up to now. The pioneering work of Kowalczyk *et al.*⁸ left the strain state of the epilayer undefined. Hashimoto *et al.*⁹ relied on a tight-binding evaluation of the shift in the core-level to valence-band-maximum (VBM) binding energy that has not been published. It is known that such calculations may deviate from measured values.¹⁰

In this paper we present an experimental determination of the variation of the band offset of InAs/GaAs with the substrate in-plane lattice constant. The outline of the paper is as follows. The second part describes the exper-

imental setup. In the third part, we report our results; they are discussed and compared with recent theoretical data.

II. EXPERIMENT

The experiments were performed in a stainless steel UHV chamber operating at base pressures below 1×10^{-10} mbar. It was equipped with a Leybold EA/200 hemispherical energy analyzer with a multichannel detector. The photoexcited electrons entered the analyzer in the direction of the sample normal and were collected with an angular acceptance of $\pm 8^\circ$. The only radiation source employed here was a differentially pumped gas-discharge lamp operating at the He I, He II ($h\nu = 21.2$, 40.8 eV), and the He II satellite ($h\nu = 48.37$ eV) spectral lines.¹¹ By analyzing the width of the Au Fermi edge, the overall energy resolution (electrons and photons) is found to be 60 meV with acceptable count rates.

The analysis chamber was interconnected through a UHV valve to a conventional Varian Mod GenII molecular-beam epitaxy (MBE) system. Freshly grown samples were transferred *in situ* to the analysis chamber via a UHV transfer chamber which was equipped with a low-energy electron diffraction (LEED) system. The MBE samples were grown on Si doped GaAs(100) wafers ($n \approx 1-4 \times 10^{18} \text{ cm}^{-3}$), S doped InP(100) wafers ($n \approx 5 \times 10^{18} \text{ cm}^{-3}$), and S doped InAs(100) wafers ($n \approx 5 \times 10^{18} \text{ cm}^{-3}$).

The experimental determination of the band offset (cf. Fig. 1) involves the measurement of the energetic separation of the Ga $3d_{5/2}$ core level in GaAs to the In $4d_{5/2}$ level in InAs across the heterojunction in question. In addition to this procedure, the core-level to valence-band-edge binding-energy differences are functions of strain¹² and have to be measured independently on samples of known strain state.

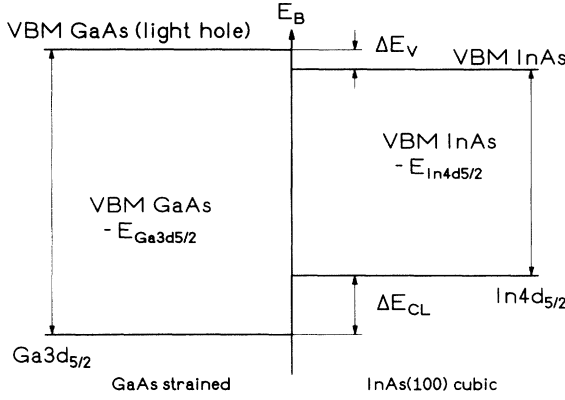


FIG. 1. Schematic energy-band diagram for GaAs strained to InAs(100). The uppermost valence band of the GaAs side is light-hole-(lh)-like.

Table I summarizes the respective growth conditions for the various samples. The V/III beam equivalent pressure ratio was 30–40 for GaAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers, for InAs layers the ratio was 10. This sometimes involved the use of two As_4 sources at different source temperatures. The $\text{In}_x\text{Ga}_{1-x}\text{As}$ buffers with x other than lattice matched to GaAs, InAs, or InP substrate were intended to be fully relaxed to their natural lattice constants. To prevent the layer from islanding, the growth temperature was as low as 420 °C.¹⁵ After deposition, the layers were annealed at 550 °C in order to ensure full relaxation. This was checked by standard x-ray diffraction measurements on the asymmetric (115) reflection of 1 μm thick layers. In order to avoid excessive band bending the buffers were moderately n doped ($n \approx 1 \times 10^{17} \text{ cm}^{-3}$). GaAs and InAs growth rates were determined by monitoring reflection high-energy electron diffraction intensity oscillations.

All epilayers are expected to be fully strained to the buffers lattice constant, since they are thinner than the critical thickness as determined for the case of thermodynamic equilibrium.¹⁴ Usually one can obtain much larger pseudomorphic layers by MBE growth at relatively low temperatures,¹⁵ thus there is no doubt that the layers were indeed fully strained. A relatively rough check that

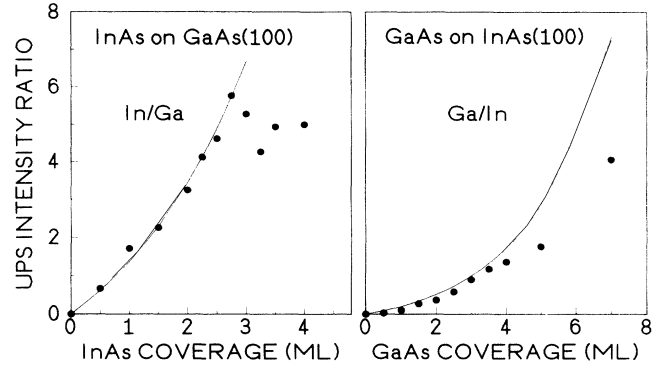


FIG. 2. Ratio of the UPS intensity of the In 4d and Ga 3d core level (dots) for the growth of the two extreme heterostructures. The solid line shows what is expected for layer by layer growth. A value of 7 Å for the mean free path and of $\sigma_{\text{In}}/\sigma_{\text{Ga}} = 2.7$ for the ratio of the respective atomic sensitivity factors was assumed.

the layers were fully strained was carried out by analyzing the separation of spots in the LEED pattern. The observed LEED reconstruction is also given in Table I.

The growth of the two extreme structures, i.e., InAs on GaAs(100) and GaAs on InAs(100), was somewhat different. By monitoring the epilayer to substrate ultraviolet photoelectron spectroscopy (UPS) intensity ratio (Fig. 2) in the range of 0.5 to 5 monolayer (ML) coverage we identified the onset of strain relaxation through three-dimensional growth. From the deviation of the experimental data points from the calculated curves for layer by layer growth (full line) we estimate the critical thickness to be 2.75 and 4 monolayers, respectively. The growth of InAs on GaAs(100) included a growth interruption of two min after every 0.25 monolayer.¹⁶

III. RESULTS AND DISCUSSION

Figure 3 exhibits a typical spectrum in the Ga 3d and In 4d core-level region for a sample consisting of 3 ML GaAs on top of 5 ML InAs on top of an $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ buffer. The spectrum originates from the He II satel-

TABLE I. Listing of all grown samples: strained “bulk” layers of InAs and GaAs and heterostructures. The respective pyrometer-calibrated growth temperature and subsequent anneal temperature in parentheses for buffer layer and the epilayers are given. All epilayers were grown at 420 °C. The observed LEED reconstruction of the epilayer is also given. The last column contains the heterostructures that have been grown on the respective buffer. They consisted of 3 ML of one material on top of 5 ML of the other one grown at 420 °C.

Substrate	Buffer growth	Epilayer growth	LEED	Heterostructures
GaAs(100)	GaAs, 580 °C	GaAs	c(4×4)	InAs (<3ML) on GaAs
InP(100)	$\text{In}_{0.17}\text{Ga}_{0.83}\text{As}$, 420(550) °C	5,10,15 ML GaAs	c(4×4)	InAs on GaAs
InP(100)	$\text{In}_{0.37}\text{Ga}_{0.63}\text{As}$, 420(550) °C	4,8,12 ML GaAs	c(4×4)	both
InP(100)	$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, 550 °C	5,7,9,11 ML GaAs 5,7,9,11 ML InAs	c(4×4) (3×1)	InAs on GaAs GaAs on InAs
InP(100)	$\text{In}_{0.69}\text{Ga}_{0.31}\text{As}$, 420(550) °C	4,8,12 ML InAs	(1×1)	both
InP(100)	$\text{In}_{0.84}\text{Ga}_{0.16}\text{As}$, 420(550) °C	5,10,15 ML InAs	(1×1)	GaAs on InAs
InAs(100)	InAs, 470 °C	InAs	(4×2)	GaAs (<3ML) on InAs

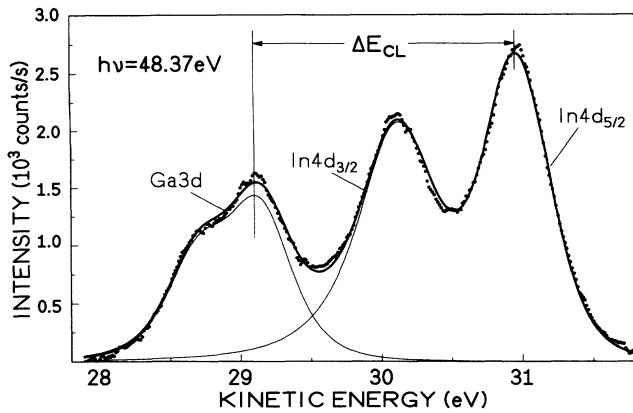


FIG. 3. UPS spectrum of a sample 3-ML GaAs/5-ML InAs/In_{0.53}Ga_{0.47}As on InP(100) together with the corresponding fit (solid line).

lite line ($h\nu = 48.37$ eV), and a linear background has been subtracted. The relative position of the Ga and In core levels was obtained by modeling a set of two doublets to our spectrum. Each doublet consists of two spin-orbit split components that are represented by a symmetric line shape containing both Gaussian and Lorentzian contributions.¹³ The spin-orbit splitting, $d_{5/2}:d_{3/2}$ intensity ratio, and the ratio of the respective full width at half maximum (FWHM) were fixed and determined by measurements on bulk samples. The position of the doublets, their absolute intensity, the FWHM, and their mixing ratio were fitted parameters.

The relative position of the In $4d_{5/2}$ core level to the Ga $3d_{5/2}$ core level as a function of the substrate in-plane lattice constant is plotted in Fig. 4. In agreement with the x-ray photoemission spectroscopy investigation of Ref. 9 the distance is constant across the whole range from the GaAs to the InAs lattice constant.

The core-level to valence-band-edge binding-energy differences were determined using the precision analysis by Kraut *et al.*¹⁷ modified to include strain effects. In this approach the position of the uppermost valence band

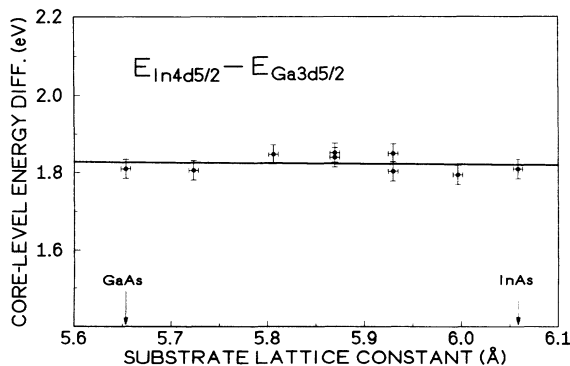


FIG. 4. In $4d_{5/2}$ to Ga $3d_{5/2}$ core-level binding-energy difference as a function of the in-plane lattice constant of the substrate on which the heterostructure was grown. The lattice constants of GaAs and InAs are marked by arrows.

at its maximum is obtained by fitting a model function to the spectrum. This model function is a convolution of a theoretical valence-band density of states with an experimentally determined UPS instrumental resolution function.

In this paper, the theoretical density of states near the valence-band edge has been calculated using results of the $\mathbf{k} \cdot \mathbf{p}$ theory. In the present case the 6×6 Kohn-Luttinger Hamiltonian for the Γ point¹⁸ including spin-orbit interaction and strain has been employed. Such a Hamiltonian has been given by People and Sputz.¹⁹ This approach, though approximate, is accurate enough to generate the band structures of the strained bulk crystal within the range that is of interest here. The resulting unstrained band structures have been checked to compare well with standard pseudopotential calculations²⁰ in the range down to 300 meV below the valence-band maximum.

The density of states is evaluated by sampling appropriately distributed random points in k space in an energy histogram.²¹ Figure 5(a) shows the theoretical valence-band-edge density of states of GaAs without any strain and before convolution with the instrumental resolution function. The density of states is dominated by the heavy-hole band, and it is almost perfectly steplike. When tensile strain is applied, the light-hole band shifts upwards with respect to the average valence-band maximum thus causing the small shoulder between -0.15 and 0.0 eV in Fig. 5(b). A simple linear fit would fail to detect the true maximum. Figure 5(c) shows the theoretical valence-band-edge density of states of compressively strained InAs. Though the heavy-hole band is on top, the density of states deviates from its steplike shape due to strain effects.

We emphasize the simplicity of these calculations as compared to, e.g., an empirical pseudopotential calculation of the whole valence density of states, and yet they

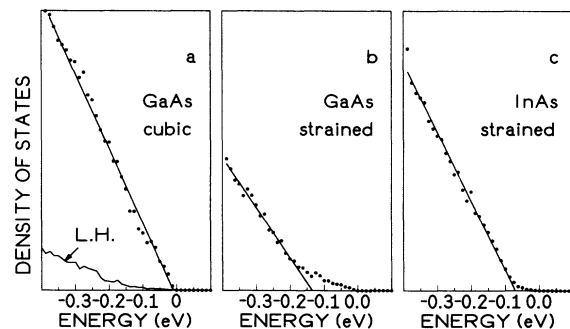


FIG. 5. Calculated density of states near the valence-band maximum before convolution with the instrumental resolution function. GaAs(100) without any strain (a), GaAs strained to the InP(100) lattice constant (5.869 Å) (b), and InAs strained to the InP(100) lattice constant (c). The dots represent the calculated density of states (resulting from the sampling of random points), the solid line gives the result of a hypothetical linear fit. For the case of cubic GaAs an arrow indicates the small part of the density of states resulting from the light-hole band.

contain all necessary details for an accurate determination of the valence-band edge. All empirical parameters, i.e., the Luttinger parameters and relative deformation potentials, are known with a sufficient degree of accuracy.

How do we know that the spectrum actually probes states at Γ ? Though UPS spectra of well-ordered crystals are dominated by direct transitions, they show in addition features like the valence-band maximum. This is mainly due to emission through evanescent states that are at a surface always available for coupling to initial states. This fact can be explicitly proven by comparing core-level to valence-band-maximum binding-energy differences as measured with different photon energies: For example, with monochromatized Al K_{α} radiation — where the \mathbf{k} conservation is destroyed and the spectrum reveals the density of initial states — the unstrained Ga $3d_{5/2}$ to GaAs valence-band-maximum binding-energy difference was 18.61 eV. This is within 30 meV of the UPS result [He II, cf. Fig. 7(a)] and published data.²²

In order to prevent any contribution from occupied surface states the fitting interval ended as close as 300 meV below the valence-band maximum. According to Ref. 17 the results are independent of surface states if these are properly excluded. This should be the case for the As-rich GaAs(100) $c(4 \times 4)$ reconstruction, where the highest-lying surface state is placed between approximately -1.0 and -0.5 eV below the valence-band edge.²³ The As-rich InAs(100) surface has not been studied with respect to this, but in view of comparative results on other surface orientations²⁴ we do not expect it to be much different from GaAs. Neither do we expect any effects on surface states due to bulk strain.

Figure 6 exhibits a typical measured valence-band-edge spectrum together with the corresponding fit. It originates from a GaAs layer strained to the InP lattice constant. The photoelectrons were excited with the He II line. The appropriate model function is the convolution of the theoretical density of states of Fig. 5(b) with the experimentally determined instrumental resolution function. In a different procedure the spectra of the valence-band edge may also be fitted with linear sections; in this

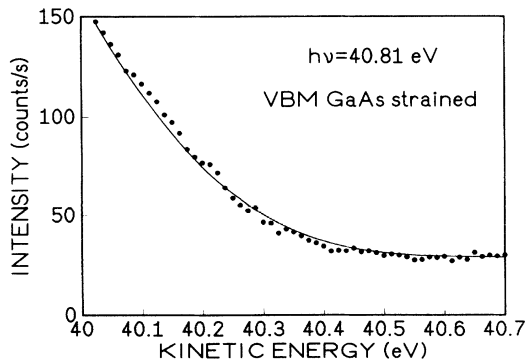


FIG. 6. Extended UPS spectrum of the valence-band maximum of GaAs strained to the InP(100) lattice constant together with the corresponding fit (solid line). The appropriate model function is the convolution of the theoretical density of states of Fig. 5(b) with the instrumental resolution function.

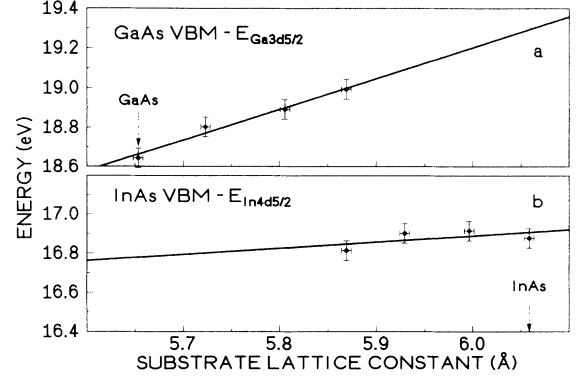


FIG. 7. Valence-band maximum to the respective core-level binding-energy differences for strained GaAs (a) and InAs (b) layers as a function of the substrate in-plane lattice constant.

case, one has to correct the results according to hypothetical fits of the theoretical density of states as those of Fig. 5. Both attempts give the same results within some ten meV.

In Fig. 7(a) the Ga $3d_{5/2}$ to GaAs VBM binding-energy difference is plotted as a function of the in-plane lattice constant. Figure 7(b) is the equivalent for the In $4d_{5/2}$ to InAs VBM binding-energy difference. In this case the hydrostatic part of the strain partly compensates for the uniaxial splitting of the bands, which explains the small variation observed. The results of Fig. 7 can be extrapolated and combined with the core-level separation to gain as the final result the InAs/GaAs valence-band offset as a function of the substrate in-plane lattice constant. Due to the extrapolation the error is larger towards the two extreme points and smallest at the InP lattice constant ($a_{||}=5.869$ Å). Obviously, by choosing an appropriate substrate, the valence-band discontinuity at the InAs/GaAs heterojunction can be varied from -40 ± 100 meV to -570 ± 100 meV. One should, however,

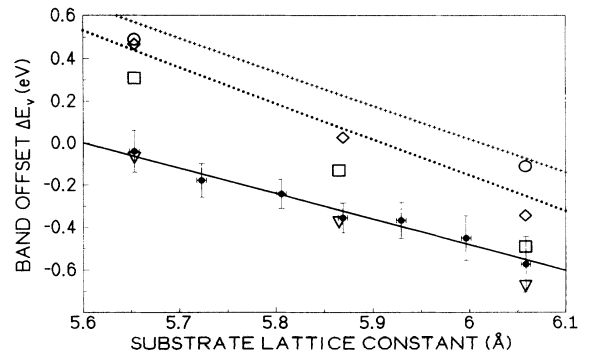


FIG. 8. Valence-band offset of the InAs/GaAs heterojunction as a function of the substrate lattice constant. The negative sign means that the topmost valence band of InAs is lower than the topmost valence band of GaAs. The solid line and error bars give our experimental results. Dotted line: model solid theory (Ref. 4). Dashed line: (Ref. 25). ∇ : *ab initio* pseudopotential (Ref. 6). \square : empirical pseudopotential (Ref. 7). \diamond : Tight binding (Ref. 5). \circ : *ab initio* pseudopotential without taking into account the interlayer separation of minimal energy at the interface (Ref. 6).

keep in mind that the respective band structures change according to the strain state of the individual layer.

In Fig. 8 we compare our results with recent theoretical investigations. As for the full self-consistent calculations of the interface, our data coincide with the *ab initio* pseudopotential calculation of Oloumi and Matthai.⁶ In their paper, Oloumi and Matthai pointed out that their results were critically dependent on the interface interlayer separation. For instruction we have also plotted the results from the same authors when the interface interlayer separation was assumed to be the average of the two bulk materials. The interface interlayer separation was not as crucial in the empirical pseudopotential calculation of Ref. 7 and has not been investigated in Ref. 5. Van de Walle was himself very cautious about the limitations of the “model solid theory” with respect to polar interfaces;⁴ indeed no theory that relies on intrinsic reference levels can account for additional interface dipoles that originate from atomic rearrangements.

Recently another *ab initio* pseudopotential calculation has been reported.²⁶ In that work, the valence-band offset is found to depend only weakly on the interface interlayer separation, the absolute value, however, differing from the results of the present paper.

IV. CONCLUSION

We have measured a large strain-induced change in the valence-band offset of InAs/GaAs heterojunctions. One can alter the valence-band offset by 530 meV on going from the GaAs to the InAs lattice constant. Our study includes a measurement of the core-level to valence-band-maximum binding energy. To account for the true shape of the density of states near the valence-band edge we used results of $\mathbf{k} \cdot \mathbf{p}$ theory. This method, though approximate, is accurate enough and avoids a full empirical pseudopotential calculation. By comparison with theory, we have been able to show that the interlayer separation at the interface is crucial for the band lineup at polar heterojunctions.

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- ¹ E. P. O'Reilly, *Semicond. Sci. Technol.* **4**, 121 (1989).
 - ² M. Cardona and N. E. Christensen, *Phys. Rev. B* **35**, 6182 (1987).
 - ³ E. T. Yu, E. T. Croke, and T. C. McGill, *Appl. Phys. Lett.* **56**, 569 (1990).
 - ⁴ C. G. Van de Walle, *Phys. Rev. B* **39**, 1871 (1989).
 - ⁵ C. Priester, G. Allan, and M. Lannoo, *Phys. Rev. B* **38**, 9870 (1988).
 - ⁶ M. Oloumi and C. C. Matthai, *J. Phys. Condens. Matter* **2**, 5153 (1990).
 - ⁷ A. Taguchi and T. Ohno, *Phys. Rev. B* **39**, 7803 (1989).
 - ⁸ S. P. Kowalczyk, W. J. Schaffer, E. A. Kraut, and R. W. Grant, *J. Vac. Sci. Technol.* **20**, 705 (1982).
 - ⁹ Y. Hashimoto, K. Hirakawa, K. Harada, and T. Ikoma, *J. Cryst. Growth* **111**, 393 (1991).
 - ¹⁰ R. W. Grant, J. R. Waldrop, E. A. Kraut, and W. A. Harrison, *J. Vac. Sci. Technol. B* **8**, 736 (1990).
 - ¹¹ J. A. R. Samson, *Techniques of Vacuum Ultraviolet Spectroscopy* (John Wiley & Sons, New York, 1967).
 - ¹² J. Tersoff and C. G. Van de Walle, *Phys. Rev. Lett.* **59**, 946 (1987).
 - ¹³ R. D. B. Fraser and E. Suzuki, *Anal. Chem.* **41**, 37 (1969).
 - ¹⁴ P. Voisin, *Proc. SPIE* **861**, 88 (1988).
 - ¹⁵ M. Gendry, V. Drouot, C. Santinelli, and G. Hollinger, *Appl. Phys. Lett.* **60**, 2249 (1992).
 - ¹⁶ O. Brandt, L. Tapfer, K. Ploog, M. Hohenstein, and F. Phillipp, *J. Cryst. Growth* **111**, 383 (1991).
 - ¹⁷ E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, *Phys. Rev. B* **28**, 1965 (1983).
 - ¹⁸ J. M. Luttinger and W. Kohn, *Phys. Rev.* **97**, 869 (1955).
 - ¹⁹ R. People and S. K. Sputz, *Phys. Rev. B* **41**, 8431 (1990).
 - ²⁰ J. R. Chelikowsky and M. L. Cohen, *Phys. Rev. B* **14**, 556 (1976).
 - ²¹ D. Brust, *Energy Bands of Solids*, Vol. 8 of *Methods in Computational Physics* (Academic Press, New York, 1968).
 - ²² R. W. Grant, E. A. Kraut, S. P. Kowalczyk, and J. R. Waldrop, *J. Vac. Sci. Technol. B* **1**, 320 (1983).
 - ²³ P. K. Larsen, J. H. Neave, J. F. van der Veen, P. J. Dobson, and B. A. Joyce, *Phys. Rev. B* **27**, 4966 (1983).
 - ²⁴ J. L. A. Alves, J. Hebenstreit, and M. Scheffler, *Phys. Rev. B* **44**, 6188 (1991).
 - ²⁵ A. Qteish and R. J. Needs, *Phys. Rev. B* **45**, 1317 (1992).
 - ²⁶ N. Tit, M. Peressi, and S. Baroni, *Phys. Rev. B* **48**, 17 607 (1993).