Local Interface Composition and Band Discontinuities in Heterovalent Heterostructures

R. Nicolini, L. Vanzetti, Guido Mula,* G. Bratina, L. Sorba,† and A. Franciosi,‡
Laboratorio Tecnologie Avanzate Superfici e Catalisi del Consorzio-Interuniversitario di Fisica della Materia, Area di Ricerca, Padriciano 99, I-34012 Trieste, Italy
and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

M. Peressi
Dipartimento di Fisica Teorica, Università di Trieste, I-34014 Trieste, Italy

S. Baroni and R. Resta
SISSA-Scuola Internazionale Superiore di Studi Avanzati, I-34014 Trieste, Italy

A. Baldereschi
Institut Romand de Recherche Numérique en Physique des Matériaux, PHB Ecublens, CH-1015 Lausanne, Switzerland

J. E. Angelo and W. W. Gerberich
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455
(Received 9 July 1993)

The local Zn/Se relative concentration at the interface in ZnSe-GaAs(001) heterostructures synthesized by molecular beam epitaxy was found to be controlled by the Zn/Se flux ratio employed during the early growth stage of ZnSe on GaAs. Correspondingly, the valence band discontinuity varies from 1.20 eV (Zn-rich interface) to 0.58 eV (Se-rich interface). Comparison with the results of first-principles calculations suggests that the observed trend in band offsets is related to the establishment of neutral interfaces with different atomic configurations.

PACS numbers: 79.60.Dp, 68.55.Bd, 73.40.Kp, 81.15.Ef

Heterovalent semiconductor heterojunctions present new challenges to our understanding of the properties of semiconductor interfaces [1], and have important potential applications in optoelectronics [2]. Carrier injection and confinement in heterojunctions is largely determined by the valence and conduction band discontinuities [3]. Recent linear response theory results suggest [4] that, unlike isovalent systems such as AlAs-GaAs, heterovalent heterojunctions, such as ZnSe-GaAs, may exhibit band offsets which depend on the detail of the atomic structure and composition of the interface. We present here a first example of the systematic relation between interface composition and band discontinities in a heterovalent heterojunction.

We selected the ZnSe-GaAs(001) heterojunction as a test system, in view of the good lattice match of ZnSe and GaAs, and the potential technological importance of these interfaces in blue emitters [2]. The large valence band offset reported for ZnSe-GaAs interfaces, in which the valence band maximum of GaAs may lay as much as 1.1 eV above that of ZnSe (Ref. [5,6]), hinders hole injection from the III-V substrate into the II-VI overlayer. In principle, however, a whole range of different band offsets may derive from the establishment of different atomic-scale interface configurations [1,4]. We have examined some of the simplest configurations for ZnSe-GaAs(001) as shown in Fig. 1, viewed in the $(\bar{1}10)$ plane. Configurations *A* and *B* correspond to mixed Se-As and Zn-Ga planes, respectively, with 50-50 compositions at the interface. Configuration *C* includes two mixed planes in sequence with Se-As 25-75 and Zn-Ga 75-25 compositions, respectively, between the Ga-terminated GaAs substrate and the Se-terminated ZnSe overlayer. Configuration *D* is the complementary configuration, with

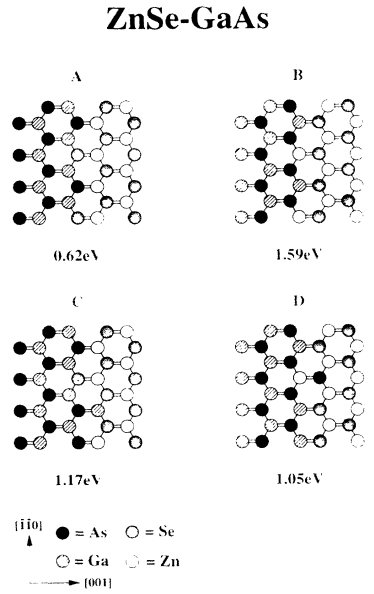

FIG. 1. Some of the simplest atomic configurations that would give rise to neutral ZnSe-GaAs(001) interfaces. Below each configuration, we show the expected value of the corresponding valence band offset, derived from first-principles electronic structure calculations.

0031-9007/94/72(2)/294(4)$06.00

Zn-Ga 25-75 and Se-As 75-25 mixed planes between the As-terminated GaAs substrate and the Zn-terminated ZnSe overlayer. Predictions for the corresponding band offsets were obtained from first-principles self-consistent-field calculations within the local-density approximation to density functional theory, using plane-wave basis sets corresponding to a kinetic energy cutoff of 12 Ry, and supercells containing 12 or 24 atoms [4]. We employed norm-conserving pseudopotentials with nonlinear core corrections for Zn and Ga, along the lines described in Ref. [7].

The predicted valence band offsets are shown directly below each interface configuration. Configurations *A* and *B* would correspond to offsets of 0.62 and 1.59 eV, respectively. Configurations *C* and *D* have no ionic dipole, as would be the case for the abrupt interface with nonpolar (110) orientation, and would correspond to valence band offsets of 1.17 and 1.05 eV, respectively. Within linear response theory (LRT), that justifies the theoretical alchemy (TA) approach by Harrison [1] and gives a prescription for the dielectric constant to use, the calculated offsets would be 0.65 eV (configuration *A*) and 1.59 eV (configuration *B*). For configurations *C* and *D*, the offsets would be equal to one another and to the offsets for abrupt, (110)-oriented interfaces (1.11 eV). The formation of antisite defects may also lead to neutral interfaces, and is expected to yield offset values similar to those obtained for abrupt, (110)-oriented interfaces.

The possible existence of a 1-eV-wide range of band offsets resulting from different interface configurations was explored using molecular beam epitaxy (MBE). ZnSe-GaAs(001) heterojunctions were fabricated on GaAs(001) semi-insulating (SI), n^+, and p^+ wafers in a two-chamber (for II-VI and III-V growth) MBE system, connected in ultrahigh-vacuum to a monochromatic (1486.6 eV) x-ray photoemission spectrometer (XPS). Undoped, *p*-doped, and *n*-doped GaAs(001)-(2×4) (As-stabilized) buffer layers 0.5 μm thick were grown on the three types of wafers using the methodology described in Ref. [8]. ZnSe epitaxial layers were grown at 290 °C using elemental Zn and Se effusion cells. The Zn/Se beam pressure ratio (R_{BP}) was monitored by means of a nude ion gauge. All of the ZnSe layers grown with $R_{BP} \geq 1$ exhibited $c(2\times2)$ reflection high energy electron diffraction (RHEED) patterns, while those grown with $R_{BP} < 1$ showed a 2×1 reconstruction [9,10].

In Fig. 2 we show experimental results for the interface composition of ZnSe-GaAs(001) heterojunctions grown by MBE at the same growth temperature of 290 °C, but with different beam pressure ratios (BPR's). We plot the experimental Zn/Se ratio *R* as determined *in situ* by XPS from the integrated emission intensity of the Zn 3*d* and Se 3*d* core levels as a function of ZnSe thickness [11], for BPR's ranging from 0.1 (solid squares) to 10 (open squares). The values of *R* were normalized to the value observed in all ZnSe bulk standards, irrespective of the BPR. The results in Fig. 2 show that while stoichiometric ZnSe films are obtained for all BPR's for high enough layer thicknesses, relatively large deviations of *R* from unity are observed in the early growth stage. High Zn (Se) overpressures correspond to Zn-rich (Se-rich) values of *R* in the early growth stage.

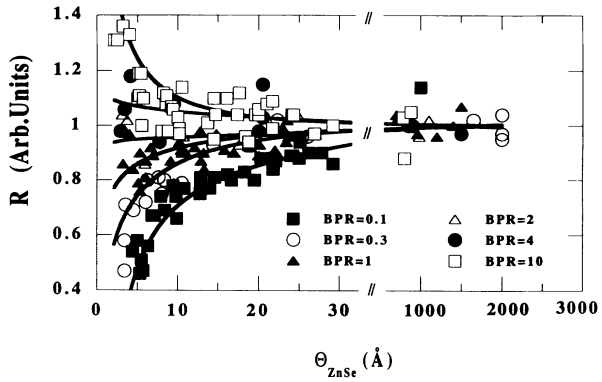

FIG. 2. Experimental Zn/Se photoemission intensity ratio *R* in ZnSe-GaAs(001) heterojunctions grown by MBE with different Zn/Se beam pressure ratios (BPR's), as a function of ZnSe thickness. Values of *R* were normalized to the value observed in all ZnSe bulk standards, irrespective of the BPR. All data were obtained *in situ* by monochromatic x-ray photoemission spectroscopy (XPS).

The atomic structure of the interface remains remarkably similar when different BPR's are employed for the growth. The structural quality of the interfaces was examined *ex situ* by means of high resolution cross sectional transmission electron microscopy (XTEM) using a Philips CM30 transmission electron microscope operating at 300 kV. In Fig. 3 we show high resolution XTEM photographs of the interface region for ZnSe-GaAs(001) heterostructures grown with $R_{BP}=4$ [Fig. 3(a)], $R_{BP}=1$ [Fig. 3(b)], and $R_{BP}=0.3$ [Fig. 3(c)]. A high degree of long range order is observed in all cases, with no evidence of the formation of a second phase [12,13] in the high resolution (Fig. 3) or (002) dark field images (not shown). The implication is that any excess Zn (or Se) present at the interface would be predominantly at substitutional positions. An order-of-magnitude estimate of the excess of Zn (or Se) that would account for the variations of *R* in Fig. 2 can be made assuming that all of the excess Zn (or Se) is at the interface, and is progressively covered by the deposition of stoichiometric ZnSe growing in a layer-by-layer mode. Submonolayer concentrations of excess Zn (or Se) are found to be sufficient to explain the observed behavior of *R*.

The band offsets corresponding to the different interface compositions were determined *in situ* by XPS from the Ga 3*d* and Zn 3*d* core level energy separation [14] (*identical* results were obtained using the As 3*d* and Se 3*d* core separation, ruling out artifacts due to chemical shifts) across the interface. As an example, we show in Fig. 4(a) results for two interfaces grown with $R_{BP}=0.1$

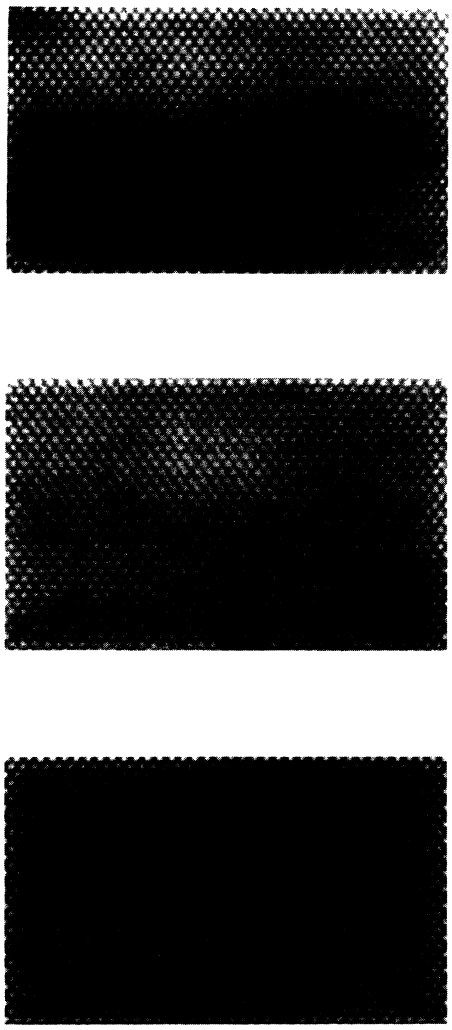

FIG. 3. High resolution cross sectional transmission electron microscopy photographs of the interface region for ZnSe-GaAs(001) heterostructures grown with $R_{BP}=4$ (a), $R_{BP}=1$ (b), and $R_{BP}=0.3$ (c).

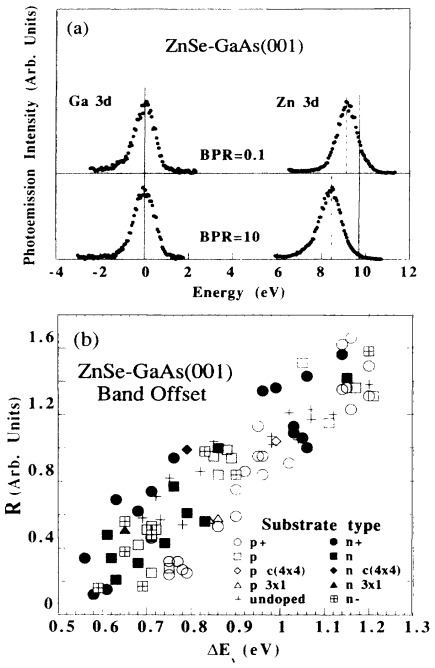

FIG. 4. (a) Representative band offset measurements in ZnSe-GaAs(001) heterojunctions, grown with different BPR's. Top: Zn 3*d* and Ga 3*d* core emission for sample grown with $R_{BP}=0.1$. The zero of the energy scale was taken at the position of the Ga 3*d* centroid, and the solid lines give the core binding energy in bulk standard (Ref. [14]). The variation in core separation (see dashed versus solid vertical line) gives directly the valence band offset. Bottom: Zn 3*d* and Ga 3*d* core emission for sample grown with $R_{BP}=10$. Note the increase in valence band offset relative to the $R_{BP}=0.1$ case. (b) Experimental valence band offset for ZnSe interfaces fabricated on GaAs(001) substrates with different type of doping. Unless noted otherwise, the substrate reconstruction was the As-stabilized 2×4 reconstruction. The offsets are plotted versus the Zn/Se ratio *R* observed for each interface in the early growth stage (at a ZnSe coverage of 3 Å).

(top), and $R_{BP}=10$ (bottom). In view of the reported atomic interdiffusion [15] and doping near the interface, three independent tests were performed to ensure that possible changes in band bending near the interface would not affect the measured core separation. The core level emission was examined for (1) photoelectron escape depths ranging from 8 to 26 Å, i.e., by gradually varying the average photoelectron collection angle from 18° to 80°; (2) ZnSe overlayer thicknesses varying from 10 to 40 Å; (3) for surface positions of the Fermi level different by as much as 0.6 eV from sample to sample, due to changes in growth parameters and photovoltage effects. No changes in core separation or individual core line shapes could be detected.

Results for a number of ZnSe interfaces fabricated on GaAs(001) substrates with different types of doping are summarized in Fig. 4(b). The valence band offsets were determined for overlayer coverages at which the ZnSe film appeared stoichiometric (25–40 Å), but are plotted in Fig. 4(b) versus the experimental value of the Zn/Se ratio *R* observed for each interface in the early growth stage, i.e., at an arbitrary ZnSe coverage of 3 Å. Maximum valence band offsets of 1.20 eV are observed for interfaces grown with the highest BPR's explored (Zn-rich case), while offsets as low as 0.58 eV are observed for the Se-rich case. The large reduction in the offset achievable as compared to published values has the potential of substantially improving hole injection efficiency in blue lasers [16].

The correlation between the interface composition in the early growth stage and the final value of the valence band offset depicted in Fig. 4(b) is remarkable, in view of the simplistic use of the parameter *R* to gauge interface composition. Such a parameter provides no information on the Ga/As ratio at the interface, which may be in

principle as important as the Zn/Se ratio in determining the overall interface composition. At XPS energies, however, only relatively small variations in the Ga/As ratio could be detected between the different interfaces, since the small interface contribution to the Ga and As core emission is superimposed in all cases on the much larger signal from the GaAs bulk.

Comparison between the experimental results of Fig. 4 and the theoretical predictions of Fig. 1 would suggest that best agreement is found for a type A interface configuration (mixed Se-As interface) when growth occurs in the high Se-rich regime. For the Zn-rich regime, good agreement between theory and experiment would be found for a type C or D interface.

Since a continuous range of offsets is observed in Fig. 4, a question may arise about the lateral homogeneity of the modified band offsets. For any intermediate value of the offset, the interface dipole responsible for the offset change must be localized in areas where the Se-As mixing (for example) has occurred and absent from areas where such mixing has not occurred. One might therefore expect inhomogeneities in the band offsets and a corresponding broadening of the core levels. Such a broadening, however, was not observed (within an experimental uncertainty of ± 0.05 eV). This may indicate a rather homogeneous distribution along the surface of the substitutional defects responsible for the offset change, so that the average distances are lower than the appropriate electrostatic potential decay length. However, we caution the reader that since the configurations examined in Fig. 1 are only some of the simplest structures which would lead to agreement between theory and experiment, we cannot rule out the formation of different substitutional interface phases with composition varying gradually with overlayer thickness. This could also explain a more homogeneous and progressive change of the band offsets.

In fact, in the absence of information on the Ga/As ratio at the interface we cannot yet prove or disprove that the interface composition is among those examined by the theory. A few preliminary results obtained for ZnSe growth on different GasAs surface reconstructions, such as the Ga-stabilized 3×1 and As-rich $c(4\times4)$ reconstructions [triangles and diamonds, respectively, in Fig. 4(b)] did not reveal an obvious dependence on the final band offsets on the *initial* composition of the GaAs surface.

This work was supported by the U.S. Army Research Office under Grants No. DAAL03-90-G-0001 and No. DAAH04-93-G-0206, and by the Center for Interfacial Engineering of the University of Minnesota under NSF Grant No. CDR 8721551.

*Also with Dipartimento di Scienze Fisiche, Università di Cagliari, via Ospedale 72, I-09124 Cagliari, Italy.

†Also with Istituto di Acustica O. M. Corbino del C.N.R., via Cassia 1216, I-00189 Roma, Italy.

‡Author to whom correspondence should be addressed.

[1] W. Harrison, J. Vac. Sci. Technol. **16**, 1492 (1979); K. Kunc and R. M. Martin, Phys. Rev. B **24**, 3445 (1981); R. G. Dandrea, S. Froyen, and A. Zunger, Phys. Rev. B **42**, 3213 (1990).

[2] M. A. Haase *et al.*, Appl. Phys. Lett. **59**, 1272 (1991); H. Jeon *et al.*, Appl. Phys. Lett. **59**, 3619 (1991).

[3] See, for example, F. Capasso *et al.*, Appl. Phys. Lett. **46**, 664 (1985); F. Capasso, Mater. Res. Soc. Bull. **16**, 23 (1991), and references therein.

[4] See S. Baroni *et al.*, in *Spectroscopy of Semiconductor Microstructures*, edited by G. Fasol, A. Fasolino, and P. Lugi (Plenum, London, 1989); A. Baldereschi *et al.*, in *Physical Properties of Semiconductor Interfaces at Sub-Nanometer Scale*, edited by H. W. Salemink (Kluwer Academic Publishers, Dordrecht, 1993); G. Biasiol *et al.*, Phys. Rev. Lett. **69**, 1283 (1992).

[5] S. P. Kowalczyc *et al.*, J. Vac. Sci. Technol. **21**, 482 (1982), examined interfaces with (110) orientation. Using the revised core positions given by J. R. Waldrop, R. W. Grant, and E. A. Kraut, J. Vac. Sci. Technol. B **5**, 109 (1987), the reported valence band offsets are 1.08 ± 0.04 eV for ZnSe deposition at room temperature followed by annealing at 300 °C, and 0.94 ± 0.04 eV for deposition at 300 °C.

[6] L. Vanzetti *et al.*, J. Cryst. Growth **117**, 573 (1992).

[7] A. Del Corso, S. Baroni, and R. Resta, Phys. Rev. B **47**, 3588 (1993).

[8] L. Sorba *et al.*, Phys. Rev. B **43**, 2450 (1991); **46**, 6834 (1992); G. Bratina *et al.*, *ibid.* **45**, 4528 (1992); A. Franciosi *et al.*, J. Vac. Sci. Technol. B **11**, 2419 (1993).

[9] G. Bratina *et al.*, Physica (Amsterdam) **185B**, 557 (1993).

[10] T. Yao and T. Takeda, Appl. Phys. Lett. **48**, 160 (1986); M. C. Tamargo *et al.*, J. Vac. Sci. Technol. B **6**, 784 (1988).

[11] The ZnSe thickness was determined from the attenuation of the Ga $3d$ and As $3d$ core emission versus deposition time. See, for example, L. Brillson, in *Basic Properties of Semiconductors*, edited by P. T. Landsberg (North-Holland, Amsterdam, 1992), p. 281.

[12] Gallium selenide-like phases were observed at the interface following ZnSe growth on As-deficient GaAs(001) surfaces: see D.-W. Tu and A. Kahn, J. Vac. Sci. Technol. A **3**, 922 (1985); D. Li *et al.*, Appl. Phys. Lett. **57**, 449 (1990); A. C. Wright and J. O. Williams, J. Cryst. Growth **114**, 99 (1991). All of our interfaces were fabricated instead on As-stabilized GaAs(001)-(2×4) surfaces.

[13] Using lower magnification and dark field imaging, virtually no line defects were observed in the samples grown with $R_{BP}=1$ and 0.3, while some threading dislocations were observed in the samples grown with $R_{BP}=4$.

[14] See G. Bratina *et al.*, J. Cryst. Growth **127**, 387 (1993). In this reference, and in the present work, the position of the Ga $3d$ and Zn $3d$ core levels in GaAs and ZnSe bulk standards was referred to the valence band maximum using a least squares linear fit of the leading valence band edge. Fits to a broadened theoretical density of states (obtained from nonlocal pseudopotential calculations) yielded consistent results.

[15] L. Kassel *et al.*, Semicond. Sci. Technol. **6**, A146 (1991); **6**, A152 (1991), and references therein.

[16] Y. Lansari *et al.*, Appl. Phys. Lett. **61**, 2554 (1992).

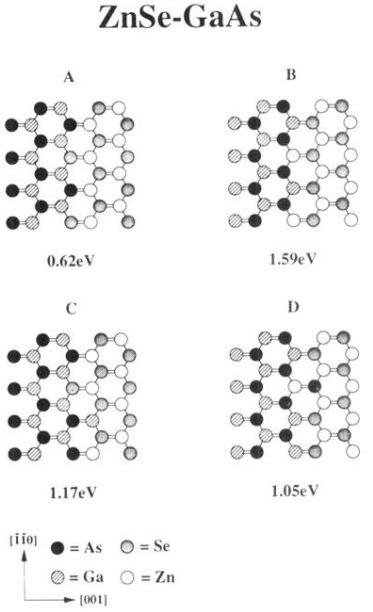

FIG. 1. Some of the simplest atomic configurations that would give rise to neutral ZnSe-GaAs(001) interfaces. Below each configuration, we show the expected value of the corresponding valence band offset, derived from first-principles electronic structure calculations.

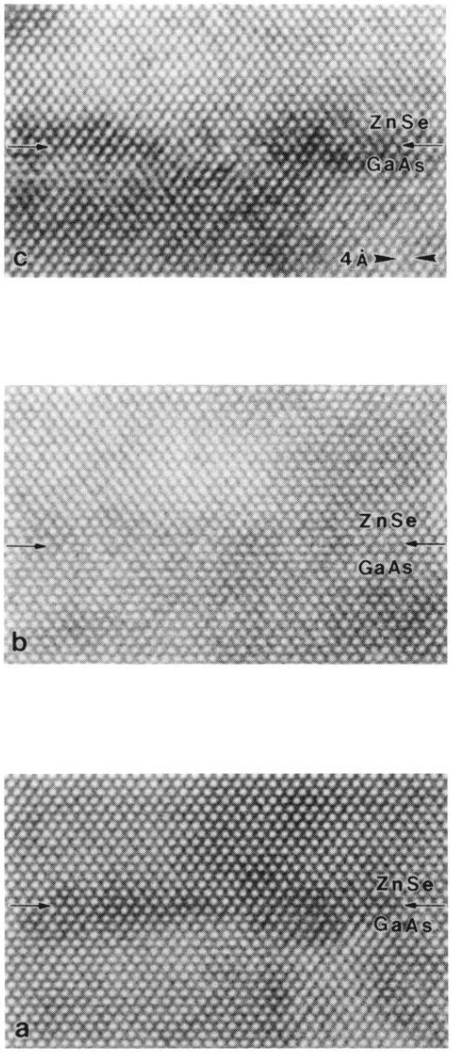

FIG. 3. High resolution cross sectional transmission electron microscopy photographs of the interface region for ZnSe-GaAs(001) heterostructures grown with $R_{BP}=4$ (a), $R_{BP}=1$ (b), and $R_{BP}=0.3$ (c).