Solving an Interface Structure by Electron Microscopy and X-Ray Diffraction: The GaAs(001)-CdTe(111) Interface

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By a combination of high-resolution imaging and grazing-incidence x-ray diffraction at the GaAs(001)-CdTe(111) heterostructure we solve the atomic structure at the interface. We measure a $\sqrt{2}(2\times 9)$ reconstructed unit cell and show that only three monolayers are involved in the interface relaxation. We deduce the first nearest neighbors of each atomic species at the interface and describe how they differ from the initial adsorbed layer on a bare GaAs(001) surface. This structure is compatible with two electrons per bond at any atom.

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The heteroepitaxial growth of compound semiconductors has recently attracted much attention for technological as well as scientific reasons. Potential applications of II-VI compounds in optoelectronics have driven an extensive and generally successful effort to grow CdTe, CdMn(Zn)Te, ZnTe, ZnSe, and ZnS [1] on various substrates including GaAs(001). The lattice mismatch should be small and the crystallographic symmetry should be preserved for a coherent growth. However, neither of these conditions is satisfied in several cases known to grow pseudoepitaxially. A typical case is the growth of (111)-oriented CdTe on GaAs(001) substrate [2]. CdTe(111) has a 0.7% misfit along the [110] direction and 14.6% along [1$\bar{1}$0]. The physical reasons for this pseudoepitaxy are not well understood. Several ideas have been suggested: The formation of an ordered precursor when selected absorption sites are occupied during the initial growth [3], the formation of an intermediate layer with intermixed species [4], or the formation of a definite compound [5]. Testing these different models experimentally is not straightforward. Incoherent and periodic interfaces are likely to involve the relaxation of a large number of atoms per unit supercell. Surface diffraction is generally not accurate enough to use directly the standard programs for crystal structure analysis at large unit cells. For instance the closely related problem of the CdTe(001) precursor on GaAs(001) recently studied by Etgens *et al.* [6] was solved for a (2×1) structure but not for the (6×1) supercell. In this Letter we show that this difficulty can be overcome by employing a new approach combining quantitative high-resolution electron microscopy (HREM) with the grazing-incidence x-ray scattering technique (GIXS). Individually neither of these techniques is new; what is new is the combination of both to solve a quasi-2D structure. As a result of this experimental study, we observe that a large supercell is formed at the interfacial planes with characteristics differing from the initial precursors.

The complementary character of the imaging and diffraction techniques can be appreciated by considering the advantages and limiting factors of both. The foremost feature of the HREM technique is its ability to give direct measurements of the respective atomic position and registry across the interface. The "phase" lost in any diffraction experiment is encoded in the image intensity. From a quantitative comparison between experimental and simulated images, the atomic position of individual atomic columns is directly deduced [7] with a resolution limit around 2 Å when atomic columns are individually resolved. In addition, periodicities and the existence of variants could be checked. By contrast, the GIXS technique has a much better resolution. In the case of a reconstructed buried interface four kinds of reflections are present, coming from the substrate, the epilayer, the truncation rods, and the interface reconstruction. In-plane information down to better than 1 Å is often available, although the out-of-plane resolution is often worse. Moreover the number of observable superlattice reflections is limited due to their small intensity compared to the background. As a consequence, the choice of the initial structure with which to start the refinement calculation is of prime importance. The previous comparison suggests a practical route to solve the interface structure. HREM provides, from two cross-sectional views [8], a first trial structure with a resolution limited to 2 Å in 3D space. In particular, it defines the number of layers involved in the relaxation at the interface, the number of atoms in each layer, and the rigid-body translation (RBT) between the two crystals. We then refine the projected structure using the in-plane x-ray diffraction data with several combinations of atom types compatible with the known crystal polarity. Using the structure giving the best fit we computer simulate HREM images and adjust the relaxation perpendicular to the interface until a good fit is obtained with the experimental images.

Our experiments were carried out as follows. The GaAs(001) surface is heated under Te pressure at 580°C forming a $(*\times 3)$-reconstructed Te-GaAs structure which is known to be one of the precursors of CdTe(111) growth [2]. A nominal 20 Å layer of CdTe is grown on this surface by molecular beam epitaxy at 320°C. This layer is protected by evaporation of a Te cap layer depos-

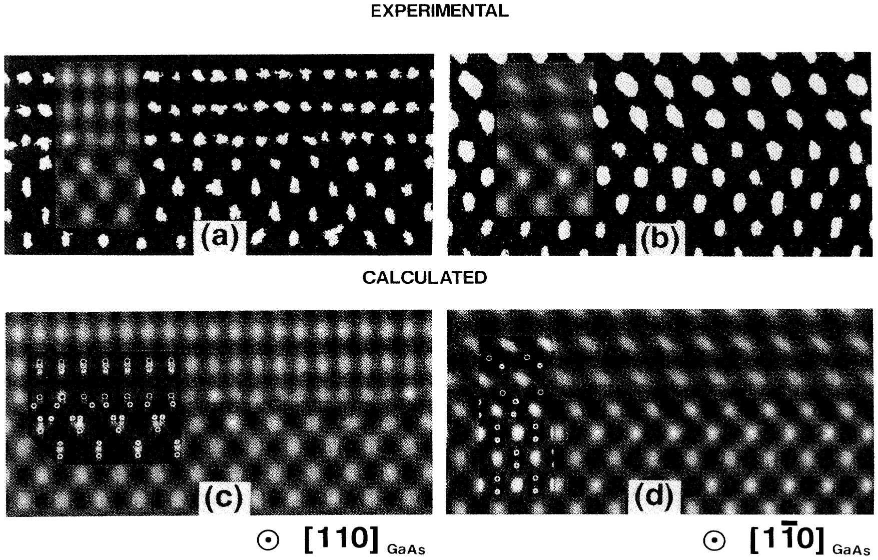

FIG. 1. Lattice image of a GaAs(001)-CdTe(111) interface along (a) [110] and (b) $[1\bar{1}0]$ of the GaAs substrate. The imaging conditions are such that atomic column pairs are encoded in white dots in (a) and black dots in (b). Calculated images (c) and (d) are computer simulated with specimen thickness equal to 60 Å and a defocus equal to -900 and -500 Å, respectively. Insets show a few atomic positions with respect to each projection.

ited at room temperature. Specimens are transferred under clean nitrogen atmosphere into the vacuum chamber of a five-circle goniometer on beam line X-16A at the National Synchrotron Light Source [9]. The in-plane diffraction intensities were recorded on several samples and averaged on several symmetry-equivalent reflections. Integrated intensities were corrected for the Lorentz factor and the variation of the area seen by the detector. Specimens were mechanically polished in [110] and $[1\bar{1}0]$ cross sections and Ar$^+$-ion milled to perforation. HREM images were taken on a JEOL 200CX high-resolution transmission electron microscope.

We first describe the results obtained by HREM (Fig. 1). In the $[1\bar{1}0]$ cross section [Fig. 1(b)] the interface appears planar and mostly coherent with no apparent supercell visible, the RBT in the [110] direction is measured to be close to zero, and most of the relaxation should occur along the observation axis as the image appears very regular and undisturbed at the interface. By contrast on a [110] cross section [Fig. 1(a)], the interface is incoherent with a periodic arrangement involving four and five GaAs unit cells, and the relaxation is directly visible at the interface with a grouping of white dots by pairs. Perpendicular to the interface, it is clear that approximately four atomic layers are involved in the relaxation: Two layers are slightly relaxed away from the CdTe(111) atomic sites and two layers are close to the GaAs(001) sites [see Fig. 3(d) for the site definition]. At this point we cannot distinguish the chemical species. However, the stacking sequence imaged by HREM combined with the crystal polarity measured by Rutherford backscattering [10], gives the following sequence for the four layers: (1) Ga in (001) sites, (2) As in (001) sites, (3) Cd in (111) sites, and (4) Te in (111) sites. It is not excluded that layer 2 or 3 be replaced by another chemical species provided they are close to (001) or (111) sites, respectively, and with the same number of atoms, i.e., eighteen for (001) and sixteen for (111) sites.

The results obtained by x-ray diffraction are as follows (Fig. 2). The bulk reflections from the epilayer show that a residual strain of 2% in the $[1\bar{1}0]$ direction is still present. In addition the in-plane diffraction pattern contains superlattice reflections clearly coming from the buried GaAs-CdTe interface. We observe them independently of the surface state (with or without the cap layer) and the integrated intensities along the superlattice rods decrease with the out-of-plane component L. This de-

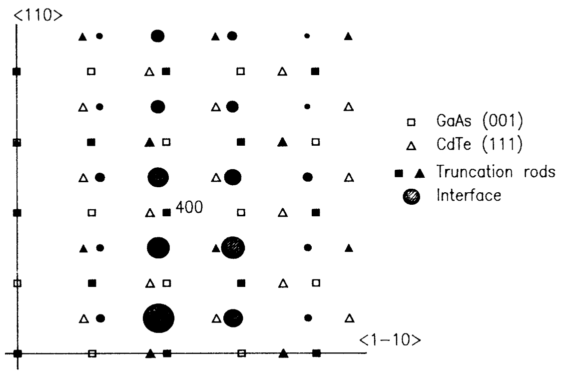

FIG. 2. In-plane ($L=0$) diffraction pattern obtained by grazing-incidence x-ray scattering ($\alpha=0.3°$). The diameter of each individual superlattice reflection is proportional to its amplitude after averaging over several symmetry-equivalent reflections.

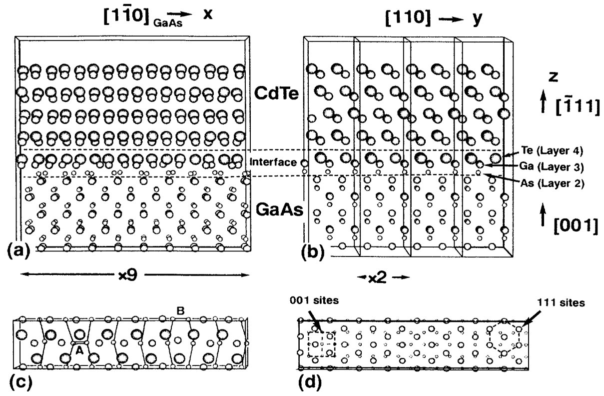

FIG. 3. Perspective view of the GaAs(001)-CdTe(111) interface as determined after relaxation of the three layers belonging to the interface. (The four possible variants of this structure are introduced in the refinement procedure.) Viewing axes along (a) [110], (b) [1$\bar{1}$0], (c) [001] GaAs. Estimated accuracy for atomic positioning is 0.02 Å along x and y and 0.2 Å along z. Projections of the (111) and (001) sites are sketched at (d) for two superimposed perfect crystals. The $\sqrt{2}(2\times9)$ unit cell is 7.99 Å×35.9 Å.

crease is compatible with a relaxation of three to four atomic layers at the interface but not with a truncation rod. These two observations point at an interfacial supercell and not to a purely surface reconstruction. All observed superlattice reflections belong to a $\sqrt{2}(2\times9)$ unit cell. The nine units along the [1$\bar{1}$0] direction are compatible with the HREM images. The two units along the [110] are not evidenced by HREM from which we deduce that the cell has a glide symmetry element along the observation axis, i.e., [110]. Among the 312 superlattice reflections which were looked for and measured, only 20 independent reflections give well-defined and measurable peaks with a dynamic of 70:1. All others were below the background intensity which originates mostly from the amorphous cap layer. However, the measured background is used to evaluate an upper limit of the structure factor F_u at this reflection. This value is incorporated in the calculation of the residual factor R [11]. We first start with trial combinations of three unrelaxed layers with atoms at (001) sites and/or (111) sites assuming a RBT along [110] equal to zero [Fig. 3(d)]. The R factor ranges from 2 to 4 and the best combination involves three layers: respectively 2, As in 001 sites; 3, Ga or Cd in 111 sites; and 4, Te in 111 sites. No improvement is obtained by the addition of other layers on either side of the interface. The R factor is drastically reduced to 0.33 by moving the As atoms off their perfect-crystal position in order to form dimers at A and B [Fig. 3(c)] with alternate translation along [1$\bar{1}$0] at $y=0$ and $y=0.5$. This creates the apparent pairing observed by HREM. The atom type of layer 3 is then adjusted and found to be Ga ($R=0.33$) rather than Cd ($R=0.63$). Further refinement is made with the conjugate gradient method with the x and y coordinates of each atom as parameters, down to $R=6.6\%$. Although the number of parameters largely exceeds the number of measured peaks, the R-factor definition incorporates the additional information on the upper value obtained for the smallest reflections. Two tests give us confidence on the reliability of the procedure: (i) Atomic relaxations along [110] remain negligible as observed by HREM, and (ii) the refinement procedure, applied to other structures, always gives a larger R factor, for instance $R=10.4\%$ if Ga is replaced by Cd. Going back to the direct space image we refine the structure perpendicular to the interface (z direction). We obtain a good fit between the experimental and simulated images (Fig. 1) for the following z values: layers 2, 3, and 4 are, respectively, at $z=0$, 1.4, and 2.33 Å. The final coordinates of each atom are employed in the perspective view of Figs. 3(a)–3(c). From the data it is easy to deduce the first-nearest-neighbor distances and the local atomic coordination (Table I). The main features of this interface structure are as follows: (i) The last layer related to the original GaAs(001) planes is an arsenic

TABLE I. Summary of the main characteristics of the local environment of individual atoms in each layer involved in the GaAs(001)-CdTe(111) interface. The range of first-nearest-neighbors (NNs) distances from the atoms of a specific layer is given in the last column. These characteristics are directly deduced from the atomic coordinates calculated in this work. Note the coordination *five* for most of the Ga atoms in layer 3 with two As and three Te as first NNs.

Layer type	z (Å)	Average number of NNs	Atom type of NNs	Distance (Å)
4 Te	2.335	4 for 13 atoms	3 Ga+1 Cd	Ga=2.5 to 2.8
			or	Cd=2.87
		3 for 3 atoms[a]	2 Ga+1 Cd	
3 Ga	1.4	5 for 13 atoms	2 As+3 Te	As=2.5 to 2.6
			or	Te=2.5 to 2.8
		4 for 3 atoms[a]	2 As+2 Te	
2 As	0	4 for all	Ga, except two As-As dimers[a]	Ga=2.4 to 2.7 As=2.33

[a] These atoms are situated in the "dislocation" core.

layer with relaxation along [1$\bar{1}$0] and formation of a zigzag chain. Every four or five unit cells those chains are in antiphase position with local formation of dimers. (ii) The last substrate layer contains Ga atoms close to the CdTe(111) sites. (iii) The interface is composed of large regions with relatively uniform structural units separated by two "dislocation" lines per period associated with the As dimers. Successive dislocation core structure along [1$\bar{1}$0] are shifted by half a period. (iv) Most of the Ga atoms in layer 3 are fivefold coordinated.

We now discuss these results in the context of previous studies. The initial Ga-rich surface known to induce the CdTe(111) growth is still reflected in the interface structure. The Te atoms as shown by Tatarenko *et al.* [2] are the first adsorbed species and x-ray photoemission spectroscopy (XPS) shows numerous Ga-Te bonds, a tendency which is even more systematic when the epilayer has fully grown. Therefore some general trends observed during the CdTe initial growth are preserved after completion of a 3D epitaxial layer. However, when analyzed in more detail, the initial adsorbtion sites are strongly modified. The buried interface has no Te-As bonds as opposed to the one detected by XPS on the $(*\times 3)$ surface and no Te-Te bonds detected on the (6×1) 111 surface, another precursor of the (111) CdTe growth. Therefore the Cohen-Solal model [12] with two Te-Ga bonds and one Te-As at each Te adsorbed atom could only be a transient structure. The reason why the Ga atoms are in the Cd sites can be understood as follows: It is the only arrangement which is compatible with no net charge at the interface. We note that for Te,Ga,As with respectively 6,3,5 s and p electrons and coordination numbers 4,5,4, there are *two electrons* per bond at any atom. In the framework of the bond orbital model these electron pairs provide the dominant energy term in the cohesion energy through the filled bonding states. The sp^3 hybrid involved in the Te and As bonds are therefore still present. For Ga, although pairing is still ensured, the hybridization should be modified in order to include d orbitals. Furthermore, bond structure calculations should give more insight on the respective degree of covalent and ionic binding. Nevertheless, the observed structure is compatible with a high cohesive energy and, as a consequence, a relatively stable interface. We also note that no intermediate compound, for instance the stable Ga_2Te_3, is observed. This is in contrast with ZnSe(001) on GaAs(001): An intermediate layer of Ga_2Se_3 is formed with a (2×2) supercell at the interface [13].

More generally the implications of our work are as follows. First we have demonstrated the advantages of combining information on the same structure in real space and in reciprocal space to solve quasi-2D structures. Thus our approach can be generalized to any reconstructed interface and should be particularly attractive for incoherent interfaces in heterostructures. Second, the ability to obtain local atomic positions in an interface between multicomponent constituents should stimulate energy calculations. The stable structure of configurations similar to those found in our work is difficult to predict even with extensive calculations. The present experimental determination opens the way to feasible electronic structure *ab initio* calculations. The electron transfer and local charge induced at the interface are particular points of interest which should now be studied. Finally, we have shown that the final configuration of an interface cannot be extrapolated from the knowledge of the initial growth of the first adsorbed species. This points to the need of detailed structural studies on interfaces *per se*, in addition to the whole body of theoretical and experimental work performed at surfaces.

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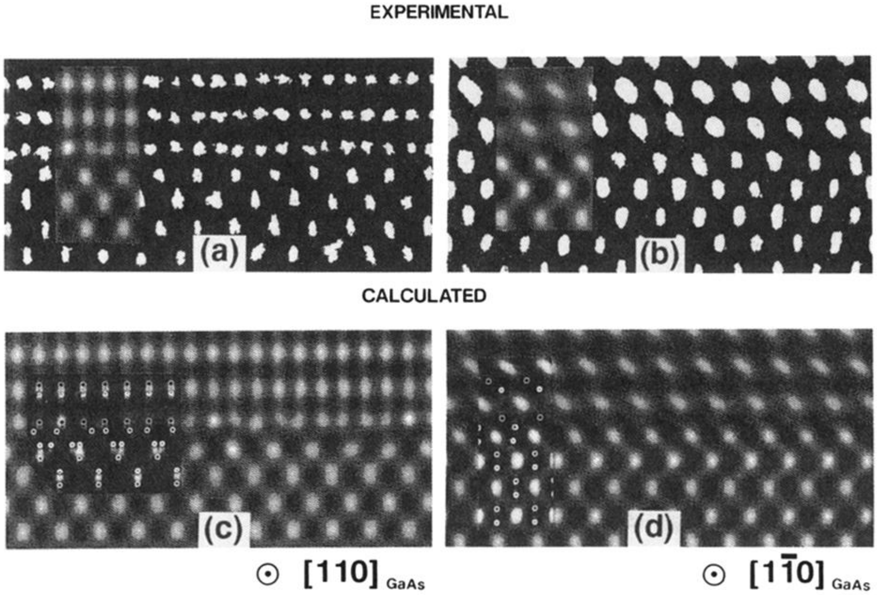

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