Imaging and manipulating heterostructure interfaces

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ABSTRACT

Epitaxial heterostructures constitute a wide variety of modern microelectronics devices. In the limit of ever decreasing feature dimensions, now entering the nanoscale in some cases, the interfaces of such devices are crucial to their operation and performance. In general the properties of the interfaces will differ significantly from those of the bulk structure of either the substrate or the heteroepitaxial film. To date, direct, non-destructive characterizations of the atomic-level structure of films and interfaces have not been readily available and this has hampered the design and optimization of heteroepitaxial devices. We describe here a novel x-ray interference method which is useful for imaging such structures with sub-Ångstrom spatial resolution while also providing chemical composition information from a map of the electron density. We illustrate the method, known as Coherent Bragg Rod Analysis (COBRA), with recent results on GaSb-InAs heterostructures of interest as infrared sources and detectors. We show that, with detailed knowledge of the interfaces from COBRA, it is now feasible to correlate specific molecular beam epitaxy growth conditions with desired electronic characteristics associated with the interface bonding. The COBRA method is quite general and only requires an epitaxial relationship between the substrate and the nanostructure that is deposited on it.

Keywords: Heterostructures, nanostructure, interfaces, infrared sensors, x-ray analysis

1. INTRODUCTION

X–ray diffraction has been a major tool for crystal structure determination for nearly one hundred years. However, there is no general solution whereby the scattering data can be directly inverted to determine the real space structure (i.e. atomic position). This is the so–called phase problem of x-ray scattering.

Recently a novel solution to the phase problem for two–dimensional (2D) crystal structures has been reported. [1] It relies on the continuous nature of the x-ray diffraction (Bragg rods) characteristic of structures that have crystallographic periodicity parallel to the substrate, but are aperiodic in the perpendicular direction (see Fig. 1). Such 2D structures are important because they include most of the materials that are relevant to electronic heterostructures such as epitaxial

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thin films and superlattices. The method of x-ray phase inversion we have developed for epitaxial materials is referred to as Coherent Bragg Rod Analysis (COBRA).

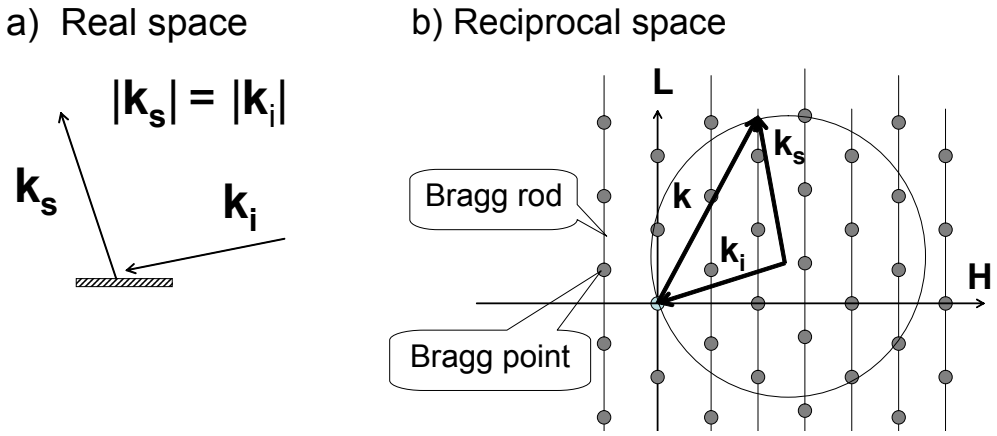

Fig. 1: (a) Scattering geometry: The incident beam with a wavevector $\boldsymbol{k_i}$ impinges on the sample surface. The sample is centered on a six circle goniometer. The scattered beam intensity with a wave vector $\boldsymbol{k_s}$ is measured by the detector mounted on the detector arm of the goniometer. (b) Reciprocal space representation of the scattering geometry: the dots represent the substrate reciprocal lattice points. The vertical lines represent Bragg rods. The circle represents the Ewald sphere. The three arrows represent incident $\boldsymbol{k_i}$ the scattered $\boldsymbol{k_s}$ and the crystal momentum transfer $\boldsymbol{k}$.

The x-ray scattering intensity profiles measured along the Bragg rods shown in Fig. 1 exhibit interference fringes as a result of the coherent superposition of scattering from the substrate and the epitaxial film. An example of such a Bragg rod scan is shown in Fig. 2. Note the very large dynamic range (more than 12 orders of magnitude between the substrate Bragg peaks and the weakest interference fringes) that is required in order to record the Bragg rod interference pattern. This quality of data acquisition requires the use of a synchrotron radiation source. In this case we took advantage of the very high brightness of an undulator insertion device[2] at the Advanced Photon Source, Argonne National Laboratory. In a COBRA structure determination approximately 10 Bragg rods are scanned in order to construct a detailed three-dimensional image of the structure, depending on the symmetry of the epitaxial structure in question.[3]

1.1. Coherent Bragg Rod Analysis (COBRA)

The COBRA method has been discussed in detail in Refs. 3 and 4. The goal is to obtain the unknown phases of the complex structure factors (CSFs) corresponding to the measured scattering intensities along the Bragg rods, in order to be able to determine the electron density distribution using a Fourier transform. The approach is summarized in Fig. 3. We begin with an initial reference structure, which is an approximate model of the structure of the sample, including the substrate. The total electron density (ED) of the sample can be decomposed into the sum of the ED of the reference structure and an unknown difference ED. Similarly, the total CSF of the sample is a sum of the CSF from the reference structure and the unknown difference.

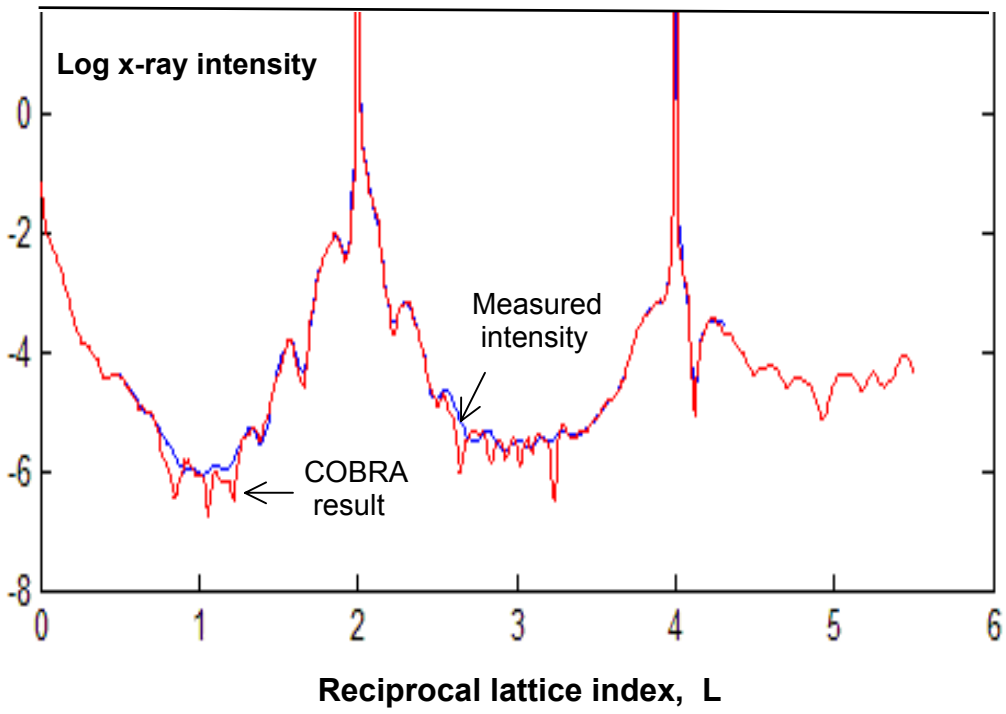

Fig. 2: Bragg rod x-ray intensity profile measured along the 20L direction of an epitaxial film of GaSb grown on a 001-oriented InAs substrate. The Bragg peaks are the intense features at L = 2 and L=4. The relevant information on the structure of the film, and its interface with the substrate, is contained in the weak interference fringes between the Bragg peaks.

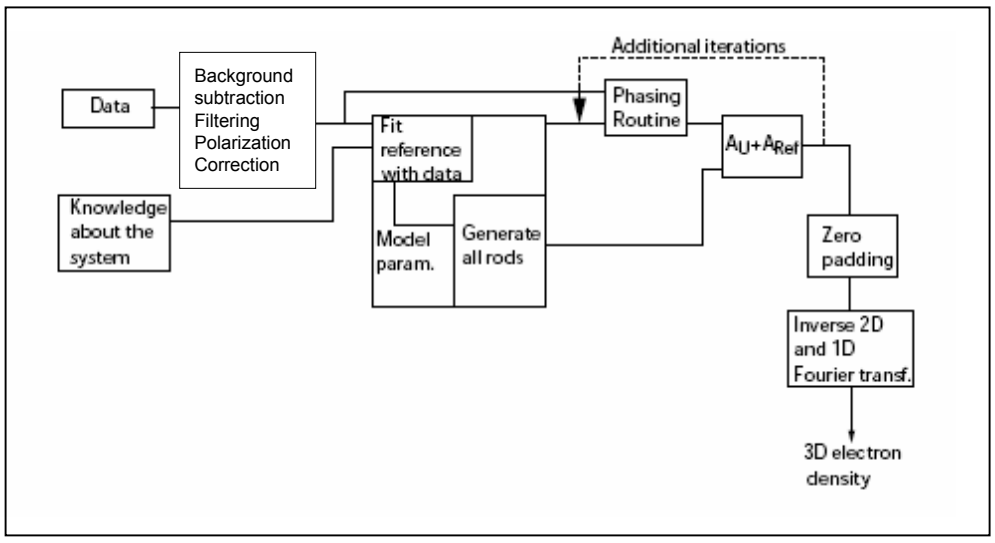

Fig. 3: Flow chart for COBRA phase inversion procedure. A_U and A_{ref} are complex structure factors of the unknown and reference structures.

The unknown difference CSFs are obtained using the experimentally measured intensities, as illustrated in Fig.2, and the calculated reference CSFs, under the assumption that the unknown CSFs vary more slowly along the Bragg rods than the reference CSF. The error associated with this assumption is diminished by taking advantage of the fact that the known part of the sample (mainly the substrate) and the unknown part (mainly the film) are spatially separated. The total CSFs are then Fourier transformed into real space, yielding a trial solution for the three-dimensional real space ED of the sample. A Gaussian window function is applied prior to Fourier transforming to reduce truncation artifacts. To be an acceptable ED, this function must be positive everywhere, zero outside the sample, and approach the known structure deep within the substrate. From the resulting ED function, we calculate scattered intensities and compare them with the measured intensities. If the agreement is unsatisfactory, the newly obtained ED is used to construct a new reference structure, and the whole procedure is iterated. Two methods are used to build the new reference structure. In the first method, the small iteration, we simply use the new ED as the reference structure. With the second method, the large iteration, we parametrize the distortions observed in the COBRA-obtained ED relative to the reference ED. These parameters are refined to obtain the best fit with the measured intensities using a standard least-squares-fitting procedure, and the resulting structure is used as the new reference structure. In the present study only two small iterations were needed to achieve convergence resulting in excellent agreement between the measured intensity profile and the COBRA-determined intensity curve as seen in Fig. 2.

The COBRA method is generally applicable to systems that are periodic in two dimensions, aperiodic in the third, and commensurate with the underlying substrate, although it can also provide detailed structural information for systems that are only partially periodic in two dimensions and are non-uniformly strained or locally incommensurate with the substrate. The result of the COBRA method is an electron density map of a single column of substrate-defined unit cells spanning across the film thickness. When the in-plane periodicity of the film is larger than that of the substrate, this ED represents the folded structure obtained by laterally translating all the atoms in the system into the column of substrate-defined unit cells using the substrate in-plane lattice vectors.

2. EXPERIMENTAL APPROACH

2.1 X-ray scattering set up

The COBRA measurements described here were performed at Sector 7 of the Advanced Photon Source, Argonne National Laboratory. The energy of the x-rays was selected by a Si (111) double-crystal monochromator with the first element cooled by liquid nitrogen. Generally speaking it is advantageous to work at high x-ray energies in order to encompass as large a range in reciprocal space as possible. This is especially important in the zinc-blende symmetry appropriate to III-V compound heterostructures where the Bragg peaks are spaced by two reciprocal lattice cells (see Fig. 2).

Use of high energy x-rays increases the spatial resolution with which the structure can be mapped. However, as noted above, the intensity of the interference fringes is quite small and can be overwhelmed by fluorescence in some cases. Normally in such measurements the fluorescence signal can be suppressed by operating the detector in pulse-height analysis mode. However, in order to ensure the very high dynamic range required for COBRA, the x-ray detector is operated in DC (current integration) mode and fluorescence suppression was not an option. Therefore the x-ray energy had to be set below the lowest binding energy for the species

present in the sample, namely E^{K1s}_{Ga} = 10.367 keV. The undulator gap was set to optimize the output at 10.25 keV. A series of calibrated x-ray attenuators in the form of Cu foils, was used in order to extend the dynamic range of the x-ray detection over roughly 12 orders of magnitude. Custom software was developed for data acquisition and control of the beamline hardware.[5]

The monochromated beam was collimated both horizontally and vertically with two sets of slits and was then focused vertically using a Rh-coated Si mirror. After conditioning, the x-ray beam size was ~400 μm (H) x 50 μm (V). A six-circle Huber goniometer was used for sample alignment, operating in Eulerian geometry.

2.2 Sample preparation

The samples described here were grown in a Molecular Beam Epitaxy (MBE) facility equipped with solid sources for Ga, and In and valved cracking cells for As and Sb.[6] The substrates were Indium-mounted on an EPI 3" sample holder. The growth rates for GaSb and InAs films on the corresponding substrates (InAs and GaSb, respectively) were calibrated by observing Reflection High Energy Electron Diffraction (RHEED) oscillations using a KSA-400 real time data-acquisition system.[7] To calibrate the Sb flux, RHEED oscillations were monitored during the growth of InSb on a GaAs substrate.

Two types of samples were grown for the purposes of this study: InAs grown on a (001) GaSb substrate, and GaSb grown on a (001)-oriented InAs substrate. In this way we could study the asymmetry present at the two types of interface and also investigate the effects of dimer and tetramer forms of the group V elements. This was achieved, at least in the case of As, by growing with the As cracker temperature set at 600°C (to produce a molecular flux rich in the As_4 tetramer) or at a cracker temperature of 1000°C which favors the As_2 dimer. The Sb cracker was fixed at 900°C resulting in a flux of Sb dimers in all experiments. The vertical atomic layer succession in the case of the InAs films was intended to be: Ga-Sb-Ga-Sb-In-As-…. –In-As; and for the GaSb films was intended to be: In-As-In-Sb-Ga-Sb-…-Ga-Sb. For each case the films had a nominal thickness of 4 unit cells.
The growth temperature for the films was nominally T_{subs} = 350°C and the growth (incorporation) rates were 0.43 ML/s for Ga; 0.32 ML/s for In; 0.63 ML/s for Sb; and 0.79 ML/s for As, as calibrated using RHEED oscillations.

3. COBRA MEASUREMENTS

3.1 InAs on GaSb

The growth of InAs on GaSb is characterized by a very sharp interface, of no more than two monolayers as evidenced by the COBRA-determined electron density profile shown in Fig. 4.

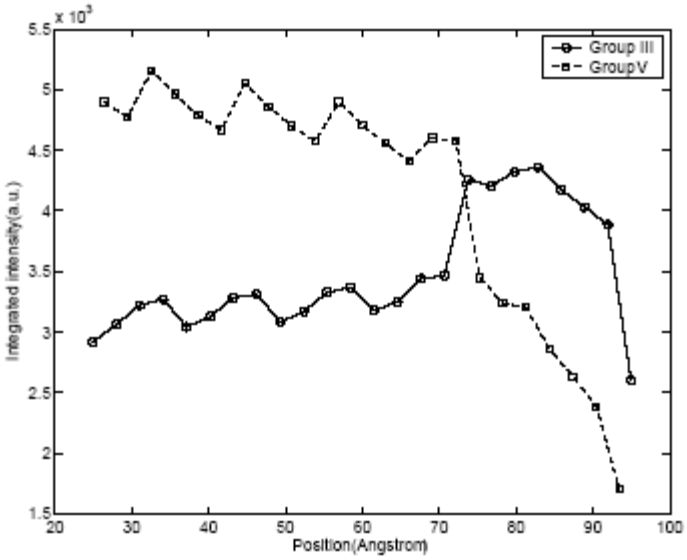

Fig. 4: Integrated electron density profiles for InAs film on 001-GaSb substrate. The two curves correspond to the Group III and Group V species. Note that the last few data points are affected by surface roughness.

The Group III density rises abruptly as InAs is deposited on the GaSb substrate, while simultaneously the Group V electron density sharply decreases. More detailed analysis [3] of the lattice spacing and chemical composition of the InAs films on GaSb confirm that the interface is atomically abrupt and that very little intermixing of species occurs at the substrate boundary. The inverse situation, GaSb on InAs, however is more interesting in that significant migration[8] does occur within the film and the interface is considerably broader. Moreover the expected[9] "InSb-like" bonding at the interface was not observed in the films prepared under the conditions used in this study. Instead, the interface bonding appears to be more "GaAs-like". It is interesting to look specifically at this case in more detail as an illustration of the power of the COBRA technique for probing atomic scale aspects of epitaxial interfaces.

3.2 GaSb on InAs

We obtained electron density profiles of the GaSb-InAs heterointerface from the inversion of Bragg rod intensity data using the COBRA phasing technique. Representative profiles for thin GaSb films on 001-InAs substrates are shown in Fig. 5. As in the case of InAs on GaSb, the interface is very abrupt, as evidenced by the sudden drop in the group III electron density [Fig. 5(a) and 5(b)] at the interface.

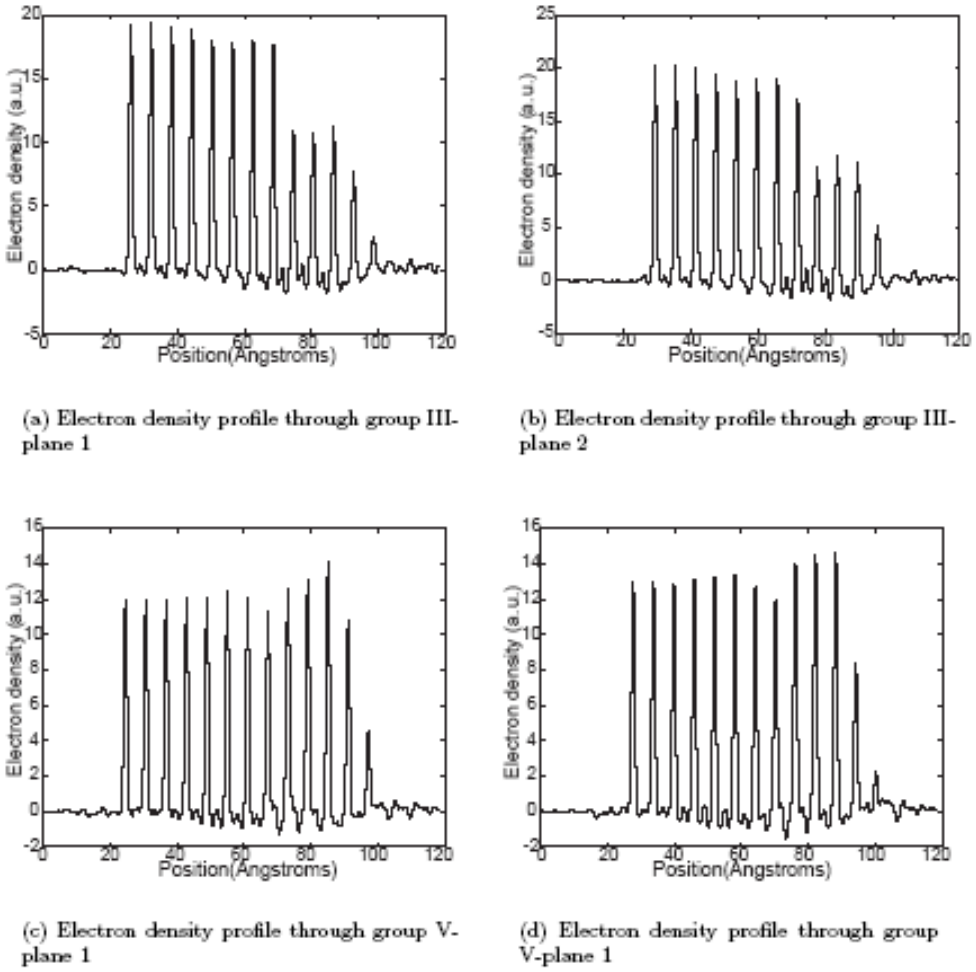

Fig. 5: Electron density profiles for GaSb film on InAs, sample. The different panels (a) – (d) show the electron density profiles perpendicular to the interface for the two planes containing the group III and group V species.

The integrated electron density for the group III and group V sites is shown in Fig. 6. Again the abruptness of the interface is apparent but now the effects of roughness are clearly seen as a tail in the Group V distribution extending towards the substrate. The origin of this broadening is further investigated by analyzing the site-specific electron density profiles in more detail.

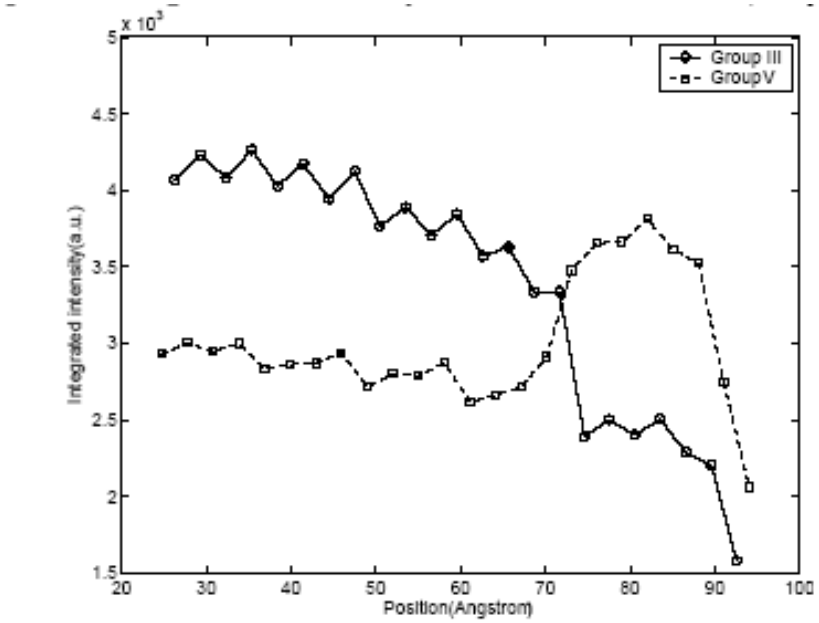

Fig. 6: Integrated electron density at Group III and Group V sites plotted as a function of position in the direction normal to the interface of the GaSb film on InAs.

By fitting the electron density peaks such as those shown in Fig. 5, and finding their centroids, the spacing between planes containing the same atomic species can be extracted from the electron density profiles. Figure 7 shows the vertical interlayer spacing determined in this way. The atomic plane spacing exhibits a pronounced dip near the interface.

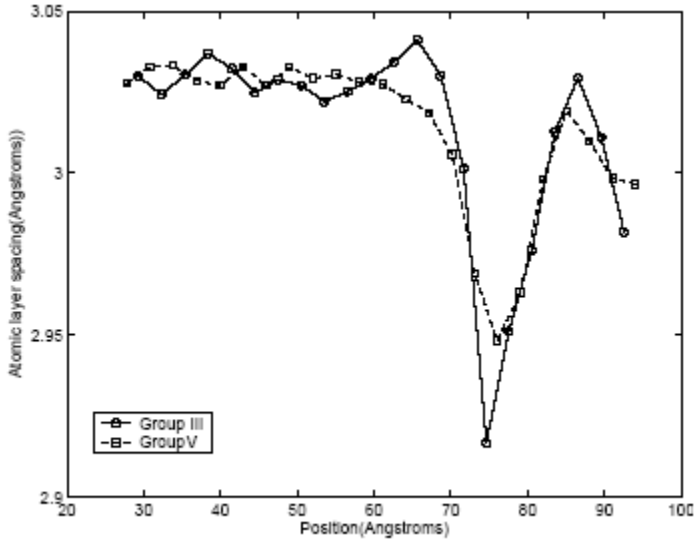

Fig. 7: Distance between atomic layers of the same type in a GaSb film on InAs.

The results shown in Fig. 7 indicate that GaSb films grown on InAs exhibit significant As presence in the film. The minimum in the lattice spacing occurs approximately 8 monolayers beneath the surface, corresponding to the depth of the interface. Note that the bulk lattice spacings of InAs (6.0584 Å) and GaSb (6.0959 Å) are very similar, whereas the value for GaAs is much smaller at 5.6532 Å. The observed dip in interplanar spacing for GaSb grown on InAs is likely associated with As migrating from the substrate surface and forming GaAs-like bonding at the interface. We see no such lattice spacing anomalies in the InAs films grown on GaSb. Migration of residual As from the chamber could also contribute to an excess concentration of As. A more detailed modeling of the composition profiles is underway. Fig. 8 shows the preliminary results of our COBRA analysis of the chemical composition profile, normal to the substrate plane, for three different films. The composition is analyzed allowing for the formation of quaternary alloys of the form $Ga_mIn_{1-m}As_nSb_{1-n}$, i.e., mixing is assumed to occur only between species in the same group (III or V). Electron density information as well as lattice spacing (assuming Vegard's law) are both needed to extract the chemical composition profile in this way.[10]

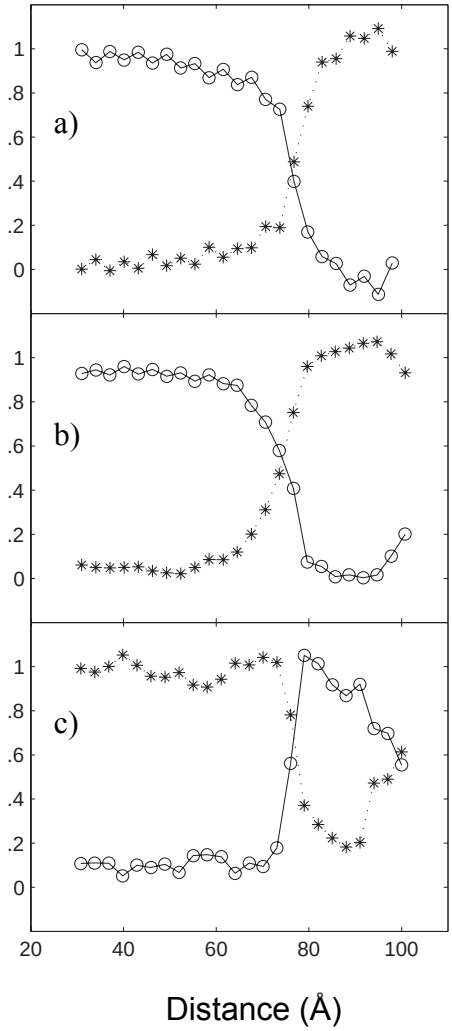

Fig. 8: Composition profiles of three different samples, as determined by COBRA. a) InAs on GaSb (with As_4 flux); b) InAs on GaSb (with As_2 flux); c) GaSb on InAs. The compositions are represented as a quaternary: $Ga_mIn_{1-m}As_nSb_{1-n}$. The solid lines correspond to m(z) and the dotted lines to n(z), where z is the distance measured normal to the interface.

The results shown in Fig. 8 (c) indicate values of n,m ≈ 0.7 at the heterointerface, corresponding to an excess of GaAs with respect to InSb. This again is consistent with the formation of GaAs-like bonding at the interface inferred from the results shown in Fig. 7. The use of As_4 (Fig. 8a) results in a slight In tail towards the substrate and As_2 (Fig. 8b) seems to promote a slightly sharper interface. These measurements indicate that control of As migration is extremely important for establishing well defined electronic and optical characteristics in these materials.

4. CONCLUSIONS

We have described the application of a new structure determination technique which is capable of mapping the three-dimensional electron density of epitaxial nanostructures. The method, Coherent Bragg Rod Analysis (COBRA), uses a direct phase inversion approach, and does not require *a priori* modeling and refinement. It can determine the location and chemical composition of the constituents of epitaxial thin films and interfaces with sub-Ångstrom spatial resolution. We illustrated the capability of COBRA with results obtained on the no-common-atom superlattice system GaSb-InAs, which is of interest as an infrared detector.[11] However, the applicability of COBRA is quite general and requires only that the film (or nanostructure) be in registry with the substrate on which it is deposited. This condition is met by a vast array of current materials that are relevant to microelectronic devices and nanostructures. The increasing importance of interfaces in such systems ensures that direct methods of structure mapping, such as COBRA, will play an important role in the future development of epitaxial nanostructures. On a broader front, one might also envision that self-assembled biostructures such a 2D protein crystals, might also be an important area for COBRA imaging.

5. ACKNOWLEDGEMENTS

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