Atomic resolution mapping of interfacial intermixing and segregation in InAs/GaSb superlattices: A correlative study

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We combine quantitative analyses of Z-contrast images with composition analyses employing atom probe tomography (APT) correlatively to provide a quantitative measurement of atomic scale interfacial intermixing in an InAs/GaSb superlattice (SL). Contributions from GaSb and InAs in the Z-contrast images are separated using an improved image processing technique. Correlation with high resolution APT composition analyses permits an examination of interfacial segregation of both cations and anions and their incorporation in the short period InAs/GaSb SL. Results revealed short, intermediate, and long-range intermixing of In, Ga, and Sb during molecular beam epitaxial growth and their distribution in the SL. © 2013 American Institute of Physics.

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Type-II superlattices (T2SLs) based on III-V semiconductors of GaSb and InAs have attracted considerable interest as an alternative to the conventional HgCdTe (HCT) detectors for mid-wavelength infrared (MWIR) and long-wavelength infrared (LWIR) laser and detector applications.1–3 T2SLs have several potential advantages over HCT detectors, such as longer Auger lifetime, reduced tunneling current, compatibility with current III-V semiconductor production, and wide band-gap tunability ranging from the mid- to long-wavelength infrared regimes.4 Both GaSb and InAs share the same zinc-blende crystal structure with a small lattice parameter mismatch. Experimentally, high-quality superlattices (SLs) free of misfit dislocations can be grown by molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD) to large thicknesses (∼1 µm).5–8 The performance of T2SLs has, however, yet to approach the theoretical predictions.9 An important structural property, critical to device performance in a layer-by-layer structure like T2SLs, is interfacial chemical sharpness.10 In particular, the InAs/GaSb quantum heterostructure has no common cations or anions, which results in different interfacial compositions of GaAs-like, InSb-like, or a mixture of InAs and GaSb. Previously, interfacial chemical sharpness and structure were studied by X-ray diffraction, bright- and dark-field (DF) transmission electron microscope (TEM),11 high-resolution (scanning) TEM (HR (S)TEM),12,13 cross-sectional scanning tunneling microscopy (XSTM),14 electron spectroscopy, and atom probe tomography (APT).13,15,16 Among these techniques, XSTM demonstrated the highest real-space resolution. XSTM is a surface sensitive technique and its application for T2SL characterization relies on detecting changes in surface electronic states associated with surface atom relaxation.17

In dark-field TEM (DF-TEM), chemically sensitive contrast is obtained and it can be used to identify interface sharpness over a relatively large sample area, but the resolution of DF-TEM is limited to ∼1 nm. Another approach proposed by Ourmazd and his collaborators uses a pattern recognition method18 to analyze HR-TEM images that contain chemically sensitive reflections, such as (200)13 in zinc-blende. In this way, they achieved lattice resolved “chemical” mapping.18 APT provides atomic concentration profiles at sub-nm resolution.18–21

Z-contrast atomic resolution imaging, achieved in a STEM using a high-angle annular dark field (HAADF) detector, is a powerful tool for interface characterization, especially for crystalline interfaces involving atoms with large atomic numbers (Z).22,23 The Rutherford scattering collected by the HAADF detector over a scanned sample area provides an intensity (I) map with peaks at the center of atoms with I ∼ Z2p (p ∼ 1 to 2).24 Recent developments in aberration correction have significantly improved the STEM resolution to sub-Å and the overall image quality has also improved.

Herein, we report a quantitative analysis of interfacial intermixing using a combination of Z-contrast imaging and APT measurements. We have improved the analysis of Z-contrast images by developing a template based image processing technique for atomic resolution chemical mapping. We apply this technique for a measurement of interfacial chemical sharpness and atomic resolution mapping of interfacial intermixing in the InAs/GaSb SL. For support and calibration, we use the APT measurements performed on the same SL using a LEAP 4000 X-Si tomograph (Cameca, Madison, WI). The HAADF-STEM imaging was performed using an aberration corrected STEMs operating at 200 and 300 kV.
The InAs/GaSb SL studied was grown by MBE on a GaSb substrate (IQE, Bethlehem, PA). A 500 nm thick GaSb buffer layer was grown on the substrate followed by a 10 nm thick AlSb layer. The SL comprised 80 periods of GaSb and InAs of nominally 8 and 14 monolayers (ML) thick, respectively. An interfacial interlayer of 1.7 ML InSb was deposited at InAs-on-GaSb interfaces for strain balance, which is after completion of a GaSb layer and before depositing the subsequent InAs layer. The SL studied herein was designed for photoluminescence (PL) measurements. By choosing 8 GaSb and 14 InAs monolayers, the SL targets the 10 μm wavelength in infrared regime, while the AlSb layer is used as a carrier barrier layer to confine photoexcited carriers within the SL. The InSb interfacial treatment promotes the formation of InSb-like bonds at InAs-on-GaSb interfaces. As our results demonstrate, no separate InSb layer is formed inside the SL. During growth, the thickness can be controlled with ±0.2 Å accuracy.

The quality of the SL was first characterized by X-ray diffraction using a Philips X’pert diffractometer (PANalytical, MA). Fig. 1(a) shows the X-ray ω−2θ scan data of the SL around the substrate (004) diffraction peak. All SL diffraction peaks between (002) and (004) were observed: only a portion of the scan is displayed. A [110] oriented cross-sectional sample was prepared by conventional mechanical polishing, followed by ion milling using 3.5 and 2.0 kV Ar ions for electron transparency utilizing liquid nitrogen cooling. Fig. 1(b) is a representative STEM image of the SL recorded along [110] using a JEOL 2200FS equipped with a CEOS probe corrector at 200 kV and medium magnification. A HAADF detector was used for recording, which gives the Z-contrast. The image displays a well-defined periodic structure of thin GaSb and InAs layers in the SL without extended defects.

A high magnification Z-contrast image of the SL with atomic resolution is presented in Fig. 2(a). This image was recorded at 300 kV and with a 0.7 Å diameter probe (at 59% probe intensity), using a probe-corrected FEI Titan HR-STEM at MINATEC, Grenoble, France. Imaged along the [110] zone axis, the closest atomic columns of cations and anions appear as dumbbell-like structures, which are separated by 1/4[001] distance. A large difference in atomic contrast between the cations and anions in both GaSb and InAs layers is observed. The Sb is brighter than Ga in the GaSb dumbbell, while In is brighter than As in InAs. This contrast is consistent with the Z-contrast expected from the HAADF detector configuration, where In and Sb have larger Z values (Z_{In} = 49 and Z_{Sb} = 51) than As and Ga (Z_{As} = 33 and Z_{Ga} = 31).

To use atomic resolution Z contrast images for quantitative interfacial analysis, we have developed a spatial averaging and image fitting technique based on template matching. The basic idea is to use two reference patterns: each contains a pair of atomic columns (dumbbell), as templates. These templates are obtained by spatial averaging well inside the layers using an iterative method. To start, one of the dumbbells is selected as the reference pattern R_L in layer L. Then the similarities between R_L and the sub-images I(i,j), where i and j are two integers that mark the location of the sub-image in the original STEM image, are measured using normalized cross-correlation coefficients C_L(i,j).25 The C_L(i,j) have values between [−1,1]. The maximum value of 1 is obtained when the intensities of R_L and I(i,j) are identical. A cross-correlation map (C-map) is then obtained. The local dumbbells whose peaks C_L are above a given threshold value (0.7 or larger) are averaged by summing the intensity in each sub-image for every pixel. These averaged sub-images defined a new reference pattern R_L. This spatial averaging is repeated several times. In each iteration, the identification of sub-images for spatial averaging is improved by increasing the threshold. The process is repeated for GaSb and InAs layers. For instance, Figs. 2(c) and 2(e) show the C-maps for the templates of GaSb and InAs. It contains peaks whose maxima determine the exact position of the dumbbells. Figs.

![FIG. 1. (a) High resolution X-ray diffraction ω–2θ scan around GaSb (004) peak. (b) Z-contrast image near substrate region obtained at an electron energy of 200 kV.](image1)

![FIG. 2. (a) Z-contrast image of InAs/GaSb superlattice and cross correlation peaks for (c) GaSb and (e) InAs regions. (b) GaSb and (d) InAs templates resulting from spatially averaging dumbbell features in respective layers.](image2)
2(b) and 2(d) show the templates obtained after spatial averaging for GaSb and InAs.

To separate the contribution of GaSb and InAs in the recorded Z-contrast images, we calculate the amplitudes \( (a_i, b_i) \) of the local images of the dumbbell, \( I(i,j) \), based on the templates

\[
I(i,j) = a_i R_1(i,j) + b_i R_2(i,j) + \epsilon(i,j). \tag{1}
\]

The local sub-image \( I(i,j) \) and the templates can be represented as vectors, and \( a_i R_1 \) and \( b_i R_2 \) represent the projections onto the respective templates \( R_1 \) and \( R_2 \) and their sum gives the projected image. In Eq. (1), \( \epsilon \) is the difference between the sub-image and the projected image. \( \epsilon(i,j) \) is ideally the remaining noise in the experimental image. A STEM image can be reconstructed, Fig. 5(a), by pasting the projected image at each local dumbbell position. The positions of the sub-images were identified by template matching using the average of GaSb and InAs as the templates. The amplitudes of \( a \) and \( b \) were obtained by linear decomposition. The results are displayed as amplitude maps for GaSb and InAs (Fig. 3). In these maps, each rectangle represents a dumbbell. By visually inspecting these maps, the sharpness of interfaces and compositions at different locations can be evaluated on an atomic scale. For example, the GaSb-on-InAs interfaces are sharper than the InAs-on-GaSb interfaces. Additionally, in the GaSb amplitude map, a significant number of GaSb peaks are detected inside of the InAs layers near the InAs-on-GaSb interfaces, which suggests chemical mixing of GaSb and InAs.

For quantitative measurement of interfacial sharpness, the amplitude line profiles of Figs. 3(a) and 3(b) were fitted with a sigmoidal function. The interfacial widths of GaSb templates, defined as the distance between 10% and 90% of the maximum plateau values, are 2.69 and 2.11 MLs at the InAs-on-GaSb and GaSb-on-InAs interfaces, respectively. The amplitude profiles of InAs templates exhibit interfacial widths that are 2.76 and 2.11 MLs at the InAs-on-GaSb and GaSb-on-InAs interfaces, respectively. Both amplitude profiles lead to the same conclusion that the GaSb-on-InAs interface is sharper than the InAs-on-GaSb interface, which means smoother InAs surfaces than GaSb surfaces during growth.

To explore the interfacial chemistry and correlate the results of the Z-contrast image with measured local compositions, we performed correlative APT analyses of the SL. Recent developments in the technology of ultraviolet (UV) laser assisted local-electrode atom probe (LEAP) tomography have made APT an important tool for atomic concentration profiling with sub-nm spatial resolution. The specimen for APT analysis was prepared using a dual-beam focused-ion beam (FIB) microscope utilizing the lift-out and annular ion milling procedures. The APT experiment was performed employing a Cameca LEAP 4000X Si at Northwestern University, at a base temperature of 25 K and under ultra-high vacuum (<8 \times 10^{-9} Pa). The measurement was performed using UV (wavelength = 355 nm) laser assisted evaporation with the following parameters: (a) 1.4 pJ pulse\(^{-1}\); (b) pulse repetition rate of 250 kHz; (c) a specimen voltage of 6.5–8.0 kV; and (d) an evaporation rate of 0.01 pulse\(^{-1}\). We chose a small laser pulse energy to minimize surface migration of atoms and to reduce the number and size of cluster ions evaporated, therefore, obtaining a more accurate stoichiometry profile. The APT data were reconstructed using Cameca’s

**FIG. 3.** Spatial profiles of amplitude for: (a) GaSb; and (b) InAs obtained from image processing. The profiles have a strong asymmetry in the interfacial intermixing. A portion of the amplitude map is shown on top of the profile. These maps reveal the atomic sites of intermixing and their distributions.
We observed in the mass-spectra a significant number of group V cluster ions (Sb\textsubscript{x,y}, As\textsubscript{x,y}, Sb\textsubscript{x}As\textsubscript{y}) formed during evaporation. The cluster ions are decomposed and the number of individual atoms is taken into account for the reconstruction of APT data and for measurement of atomic concentrations of the different elements.

Fig. 4(a) shows a 3D reconstruction of the atomic distributions in the InAs/GaSb SL near the AlSb barrier layer: the GaSb and InAs layers are labeled. The layers appear to have similar thicknesses in the reconstruction. The InAs layers appear thinner than they should be according to the STEM results because InAs has a lower evaporation field than GaSb.\textsuperscript{13} From the reconstruction, we created atomic concentration profiles using a small volume (20\,\times\,20\,\times\,30\,nm\textsuperscript{3}) selected from the center of the 3D conical reconstruction, where the depth resolution of the APT data is the best. The concentration was density-corrected\textsuperscript{29} and the z-direction was rescaled based on the STEM results to compensate the distortion caused by lower evaporation field of the InAs layer.\textsuperscript{27} The results for each element are displayed in Figs. 4(b)–4(e). The largest concentrations measured are approximately 40, 50, 60, and 35 at. % for Ga, Sb, In, and As, respectively. The measured concentrations deviate from the ideal stoichiometry of 50:50 at. %. Some of the difference can be attributed to the difference in evaporation rates of different atoms and the formation of the cluster ions. This effect could, in principle, be corrected by performing calibration experiments using pure GaSb and InAs standards.\textsuperscript{13} For this study, we focus on the interfacial chemical sharpness and variations in the concentration ratio.

For a quantitative comparison, we fitted the APT composition profiles using the same sigmoidal function we used for STEM results. Employing the same definition for interfacial width as the distance between 10\% and 90\% relative concentrations between the plateau values, the average cation widths of Ga and In for InAs-on-GaSb and GaSb-on-InAs interface are 1.99 nm (6.5 MLs) and 0.79 nm (2.6 MLs), respectively. The average anion widths for Sb and As are 1.65 nm (5.4 MLs) and 0.59 nm (2.0 MLs) for InAs-on-GaSb and GaSb-on-InAs, respectively. Both the cation and anion profiles demonstrate that the GaSb-on-InAs interface is sharper than that of InAs-on-GaSb. The APT results reveal the same asymmetric trend as the STEM image processing results. Although its spatial resolution is poorer than the aberration corrected STEM image, APT provides quantitative concentration values. The combination of the STEM and APT results thus permits a more detailed analysis than do the two methods used independently.

Fig. 5 presents a composite view of interfacial intermixing in the InAs/GaSb SL as observed by STEM and APT. The measurements were performed on the same SL but for different volumes of the specimen. Because of this, the following discussion focuses only on the general trends in these two data sets. The image presented in Fig. 5(a) is obtained by projecting the experimental image onto the GaSb and InAs templates using the image processing described above. The reduced noise in the projected image makes it useful for identification of interfacial structure. Both the InAs-on-GaSb and GaSb-on-InAs interfaces exhibit intermediate intensity for the dumbbells. Since the image contrast is proportional to Z, an intermediate intensity indicates intermixing of Ga and In at cation sites and As and Sb at anion sites. The GaSb-on-InAs interfaces have \sim1 ML of dumbbells with intermediate intensity, while the InAs-on-GaSb interfaces display 2\sim3...
Feature II is an increase in the Ga/Sb ratio at the InAs-on-GaSb interface, which is associated with a decrease in the In/As ratio. We interpret this as the substitution of Ga for In inside the InAs layer near the As-In/Sb-Ga interface. This interpretation is supported by STEM because of the decreased intensity at the In columns. In region III, the In/As ratio is relatively constant, while there is a significant decrease in the Ga/Sb ratio. This suggests the substitution of Sb for As and a significant decrease of Ga in this region.

The above results are consistent with the cation and anion segregation of Ga, In, and Sb during MBE growth as predicted by theory. Due to surface segregation during the MBE growth process, a fraction of atoms (F) segregate in the next layer, while the remainders are incorporated into the lattice underneath. This creates an asymmetrical, decaying, concentration profile. The differences that we observe in the distributions of Ga, In, and Sb atoms can be attributed to the magnitude of F. The segregated In is largely incorporated within ~1 ML at the GaSb on InAs interface, while Ga and Sb are incorporated with ~2-4 and ~6-8 MLs, respectively, at the InAs-on-GaSb interface. The wider concentration profile of Sb in InAs is also related to the intentionally deposited InSb interlayer layer deposited on the GaSb surface. The InSb interlayer complicates the surface segregation, and therefore, a quantification of this effect would be accomplished with samples grown without the interlayer deposition.

In conclusion, we have demonstrated atomic level mapping of interfacial intermixing in a short period InAs/GaSb superlattice. This is achieved by combining atom-probe tomographic data with quantitative analyses of atomic resolution Z-contrast images. Compared to other measurement techniques, the information we present herein directly reveals composition on a sub-nano scale and at high spatial resolution demonstrating the importance of correlative experiments on the same sample. For an InAs/GaSb superlattice, we identified segregation of Sb, Ga, and In atoms and quantitatively measured their incorporation in the lattice. With the techniques we developed herein, studies comparing the segregation and intermixing at the interfaces of superlattices, with and without interfacial InSb deposition, are now possible and can lead potentially to optimally designed interfaces. The correlative approach employed herein is general and can be applied to other superlattices, including those used in devices.

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