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REVIEW ARTICLE Cross-sectional scanning tunnelling microscopy of III–V semiconductor structures

R M Feenstra

IBM Research Division, T J Watson Research Center, Yorktown Heights, NY 10598, USA

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Abstract. The method of cross-sectional scanning tunnelling microscopy (stm) is described. Illustrative examples are given of studies of III–V semiconductor systems, including Al_xGa_{1-x}As/GaAs superlattices, InAs/GaSb superlattices and low-temperature-grown GaAs. Physical properties studied include alloy clustering, interface roughness, band offsets, quantum subbands and point defects. In each case, stm permits the observation of structural features on an atomic scale. The associated electronic spectroscopy for states a few eV on either side of the Fermi level can be determined. Such information is relevant for the operation of devices constructed from these layered semiconductor systems.

1. Introduction

The method of cross-sectional scanning tunnelling microscopy (STM) has been used for studying a variety of epitaxial semiconductor structures [1-36]. Such structures generally consist of a number of layers, with thicknesses ranging from angstroms to micrometres, grown by molecular beam epitaxy (MBE) on a singlecrystal substrate. In the method, a cross section of the structure is prepared by cleaving, and STM studies are performed on this cleavage face. For layered systems (i.e. superlattices), one gains information on the interfaces between layers, as well as the properties of the individual layers themselves. Most studies to date have been performed on III-V semiconductors (GaAs and related materials), although some work has appeared on the group IV materials (Si and Ge) [31-33]. For GaAs, the cleavage face is a (110) plane, and for cleavage in ultra high vacuum (UHV) this face has the convenient property that the dangling bond energies do not lie within the bandgap. Thus, spectroscopic studies of this surface reveal bulk-like properties for the bandgap, bandoffsets and other features. Alternatively, for Si, cleavage can be accomplished on either the (110) or (111) faces, but in both cases the spectroscopy of as-cleaved surfaces is dominated by dangling bond surface states. Thus, some chemical treatment is required to passivate these states, and perfect passivation may be difficult to attain. Passivation for the GaAs cleavage face is also possible, and is a viable alternative to UHV cleaving [25].

In addition to the requirements for sample preparation discussed above, another requirement for crosssectional STM is the ability to conveniently position the STM probe tip over the epitaxial layers of interest. These layers are located, of course, at one-edge of the cleavage face. Thus, they are found by stepping the probe tip over to this edge in a controlled fashion. This stepping motion, which operates in the sub-micrometre to millimetre length range, was a limitation in implementing the technique in the early years. However, with the commercial availability of UHV-compatible piezoelectric steppers (and improved knowledge about constructing home-built versions), this no longer presents a significant problem. One other technical detail concerns detailed spectroscopic measurement. For studies of bulkrelated spectral features, a high dynamic range (about six orders of magnitude) in current and conductance is required to properly define band edges and other features. Such a high dynamic range is not attainable with a routine, quick current-voltage measurement. Thus, special techniques have been developed to acquire and analyse such spectra [17, 18].

In this paper, we review results of cross-sectional STM studies of III–V semiconductor systems. All data are thus obtained from a (110) cleavage plane of the structures. We restrict ourselves to studies performed *in situ* in UHV, although it should be noted that progress has been made in *ex situ* observations [16]. This review is not intended to be comprehensive in the reporting of all cross-sectional STM works performed to date, but rather, we provide an overview of the range of possible studies

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which can be performed, providing illustrative examples in each case. We start in section 2 with a discussion of the imaging and spectroscopy of pn junctions. Section 3 presents observations of fluctuations in composition observed in alloy materials. Quantitative interface roughness measurements are discussed in section 4. Spectroscopic measurement of band offsets is presented in section 5, and spectroscopy of quantum well subbands is shown in section 6. Observation of crystal defects is discussed in section 7, and other types of studies are mentioned in section 8.

2. pn junctions

Cross-sectional STM has been used in a number of studies to profile pn junctions and doping superlattices [8–16]. Such work has clear device applications, for example for profiling of shallow dopant implants or determining diffusion profiles, and the studies are also useful as test cases for evaluating the cross-sectional STM method itself. Contrast between n and p-type material is large and easily observed, and the spectroscopic signature of the different doping types is well understood. In addition, doping studies provide a good test vehicle for evaluating tip-induced band bending effects, as discussed below.

Figure 1 shows an STM image obtained from a pndoping superlattice, consisting of alternating layers of n- and p-type material [8]. Doping concentrations are 5×10^{19} cm⁻³ and 5×10^{18} cm⁻³ for the n- (Si-doped) and p-type (Be-doped) layers respectively. The n-type layers appear bright and the p-type layers appear dark in this constant-current image. The origin of this contrast is purely electronic (the cleavage face is atomically flat), as discussed below. Significant fluctuations in contrast can be seen, and they are attributed to the individual dopant atoms in the layers. The number of perturbations (protrusions or depressions) seen in the middle n-type layer is roughly the same as the number of dopant atoms in the surface atomic plane of that region[†]. The target thickness for both the n- and p-type layers in figure 1 was 50 nm but, as seen in the image, the n-type layers are significantly thicker, with observed average thicknesses of 67 and 32 nm respectively. The extra thickness of the n-type layers was attributed to diffusion of the Si (possibly enhanced diffusion due to its high concentration) during growth, and the presence of this diffused region was confirmed by secondary-ion mass spectrometry (SIMS).

As illustrated in figure 1, cross-sectional STM, with its ability to resolve atomic features, has a much higher resolution than SIMS. A remaining question, however, is the ability of STM to quantitatively determine dopant concentrations with high spatial resolution. One such method is to simply count the number of dopant atoms appearing in an STM image [12–14]. An example of



Figure 1. STM image of a (110)-cleaved face of GaAs, showing a doping superlattice with n- and p-type layers, Fluctuations in the layers are attributed to the presence of dopant atoms. The image was acquired with a sample voltage of -2.0 V. The relative tip height is given by a grey scale, ranging from 0 (black) to 3.5 Å (white). (From [8].)

this counting method is shown in figure 2, where we show an STM image obtained from a 1×10^{19} cm⁻³ Be-doped GaAs sample [12]. Individual dopant atoms can be clearly resolved, with their contrast in the image determined simply by considering them as charged scattering centres for the carriers in the semiconductor [20]. Thus, as for the case in figure 2 the negatively charged dopant atoms are attractive to the holes in the valence band, and the dopant atoms thus appear as protrusions. From the number and magnitude of the observed protrusions, it is concluded that dopant atoms in the top several atomic planes are being imaged. Using this method of dopant atom counting, profiles for dopant concentrations in the range $(1-15) \times 10^{18}$ cm⁻³ have been determined, as shown in figure 3 [13]. The STM results are in good agreement with SIMS measurements on the same sample. Lower dopant concentrations could probably be determined by direct counting, although for much lower values the surface areas which need to be reliably imaged become rather large.

Another method for the determination of dopant concentration involves the use of tunnelling spectroscopy. We first describe results obtained from highly doped nand p-type material, and then discuss their dependence on doping concentration. Figure 4 shows spectroscopy results obtained from n-type GaAs [17]. To achieve high dynamic range in the measurement, the conductance dI/dV is measured along a contour of varying tip-sample separation, s, and then transformed to constant tip-sample separation using the known exponential dependence of tunnel current on separation [17, 18]. The result is shown by the full curve in figure 4(a). With five to six orders of magnitude obtained in the data, we see a clear definition of the band edges, near 0 and -1.4 V.

[†] The appearance of the Si dopants in figure 1 is complicated by the fact that, at high concentrations, Si is present as both donors and acceptors in GaAs [11].



Figure 2. (*a*) STM image of a (110)-cleaved, 1×10^{18} cm⁻³, Be-doped GaAs surface. Image displays 31×29 nm of the As sublattice taken with sample voltage of -2.1 V and current of 0.1 nA. The relative tip height is given by a grey scale, from 0 to 0.2 nm. Nine hillocks (dopants) are identified using numbers at the closest point on the perimeter. (*b*) Tip height trace along the $[1\bar{1}0]$ direction of a selection of the hillocks identified in (*a*). (*c*) Scatter plot of area under the $[1\bar{1}0]$ tip height traces (integrated intensity) of all nine hillocks — note the uniform distribution. From [12].

Smaller features are also present in the spectrum, but are difficult to discern because of the logarithmic scale used in figure 4(a). Thus, a second step is performed in the analysis, normalizing the constant-s data to some quantity which acts as a 'background' subtraction on the logarithmic scale, thus suppressing the large variation in conductance arising from both the presence of the semiconductor bandgap and the voltage dependence of the tunnelling transmission term. This normalization quantity is taken to be $\overline{I_s/V}$, which is the total conductance I_s/V at constant s, broadened over an energy range of width 1.5 V. This quantity is shown by the broken curve in figure 4(a). The final form for the normalized spectrum, the ratio of differential to total conductance, is shown in figure 4(b). Similar data from p-type GaAs are shown in figure 5 [17].

A number of features are apparent in the spectra of figures 4 and 5. Valence and conduction band onsets are clearly defined, denoted by E_v and E_c respectively.



Figure 3. STM image of GaAs layers with variable dopant concentration and various depth profiles. (a) Calculated bulk band structure for the intended heterostructure. In registry below, (b) shows the topographic image, 100×50 nm in size, of the layers taken with sample voltage of -2.1 V and current of 0.1 nA. The relative tip height is given by a grey scale, from 0 to 0.2 nm. (c) Several topographic line scans across the image in (b), along the [100] direction (Al_xGa_{1-x}As layers vertically aligned); atomic corrugation shown in inset. (d) Line scan (full curve) corresponding to the averaged line scan over the top half of (b), smoothed slightly to take out atomic corrugation, and compared with the Be concentration measured by sims (dotted curve, right axis). (e) Dopant histogram determined by counting the while hillocks (dopants) in a series of rectangles across (b) (full curve, left axis) and compared with the Be concentration measured by sims (broken curve, right axis). From [13].



Figure 4. Analysed spectral data for n-type GaAs(110), showing (*a*) differential conductance at constant tipsample separation, and (*b*) ratio of differential to total conductance. The broken curve in (*a*) shows the total conductance, broadened over a voltage width of 1.5 V. The components of the spectrum are indicated in the inset: C, conduction band; V, valence band; and D, dopant induced. Valence and conduction band edges are indicated by dotted lines, labelled E_V and E_C respectively. The thin vertical line at 0.45 V marks a surface state feature. (From [17].)

The zero of voltage corresponds to the Fermi level position in the semiconductor, seen to be located at the top (bottom) of the bandgap for n-type (p-type) material. Non-zero current and conductance within the gap, the so-called 'dopant-induced' component, arises from electrons tunnelling out of filled conduction band states for n-type material or into empty valence band states for p-type material [19]. The relevant states contributing to this conductance are located very near the band edges, of course, but due to the voltage dependence of the tunnelling transmission term, contributions to the conductance from these states are seen throughout the bandgap. This D component in the conductance is a very sensitive measure of surface quality, since a small shift in surface Fermi level position due to steps or residual contamination will cause this component to disappear from the spectrum [20]. Other features which are visible in the spectra are small bumps seen on the empty-state (positive-voltage) side of the spectrum, as marked by the vertical line in figure 4(b). Such features are also seen in other III-V materials, and they are interpreted as arising from cation-derived surface states [17].

Based on the spectroscopy results presented in figures 4 and 5, the contrast between n- and p-type material is easy to understand. For imaging at positive sample bias (empty states), more states are available for tunnelling into n-type material, and thus it will



Figure 5. Analysed spectral data for p-type GaAs(110), showing (a) differential conductance at constant tipsample separation, and (b) ratio of differential to total conductance. The components of the spectrum are indicated in the inset: C, conduction band; V, valence band; and D, dopant induced. Valence and conduction band edges are indicated by dotted lines, labelled E_V and E_C respectively. (From [17].)

appear brightest (more current, or equivalently, greater tip-sample separation for constant current). Similarly, p-type material will appear brightest when tunnelling out of filled states [8][†]. These results apply to nondepleted material; near depletion regions the contrast changes significantly due to tip-induced band bending [8-11, 17, 19]. Then, more of the applied tip-sample bias is dropped in the semiconductor itself, and the current is correspondingly reduced. Thus, we expect the depletion regions will always be dark (low tunnel current) in the images, and this is indeed observed. The amount of tip-induced band bending is found to depend on surface conditions: an ideal, flat surface will be more susceptible to tip-induced band bending effects, whereas a surface with residual midgap states arising from cleavage steps or incomplete passivation can more effectively screen the electric field from the tip [10, 25].

The above effects of tip-induced band bending provide another means of determining dopant concentration. For semiconductors in depletion (positive sample bias for n-type material or negative bias for p-type), the amount of tip-induced band bending will increase as the doping concentration decreases. This increased band bending will, in turn, cause the current to decrease for constant tip-sample separation, or alternatively the tip-sample

[†] The D-component in n-type material may complicate the appearance of pn layers at negative sample bias, since, under suitable conditions, it can be as large as the V-component in the p-type material [8].

separation to decrease for fixed current. Such effects have been seen in a number of studies [10, 11, 13]. In particular, the study of Johnson *et al* shown in figure 3 also included examination of the tip height across the varying doped regions. The tip height was found to be proportional to the logarithm of the doping concentration as determined by SIMS, as seen in figure 3(d).

3. Alloy fluctuations and clustering

Perhaps the major application of cross-sectional STM is the study of semiconductor superlattices. The superlattices are generally grown using alloy systems (ternary or quaternary), which allow greater flexibility in adjusting the lattice constant and bandgap. One such system is $Al_xGa_{1-x}As/GaAs$, which has been studied by Salemink and co-workers [5, 21–24] and by Shih and co-workers [25, 26]. In this section we discuss the observation of spatial fluctuations in the average alloy composition due to clustering of the atomic species. The related issue of interface roughness is discussed in the following section.

Figure 6 shows an STM image of a 10 nm thick $Al_{0.3}Ga_{0.7}As$ layer surrounded on both sides by GaAs layers [24]. On average, the $Al_{0.3}Ga_{0.7}As$ layer appears



Figure 6. (*a*) sTM image of 10 nm wide $AI_xGa_{1-x}As$ layer, surrounded on both sides by GaAs. Topographic image with relative tip height given by grey scale from 0 (black) to 0.38 nm (white). Two (112) directions are indicated. (*b*) Topographic line scans along rows 61, 65 and 69 are indicated. The positions of the half-maximum of the $AI_xGa_{1-x}As$ layer are indicated by HM. (From [24].)

darker than the GaAs, but distinct variations in the contrast are apparent. (The very dark spots seen in the image arise from missing As atoms at the surface, as often seen on these (110) cleavage faces.) In this filled state image it is the As sublattice which is imaged. The observed variation in the magnitude of the As corrugation is attributed to the number of Al atoms which are bonded to the surface As atom. Because the Al-As bond is more ionic than the Ga-As bond, Al nearest neighbours result in more charge being transferred to the nearest As sites. This lowers the energy of the Asrelated surface state, and thus those As atoms appear darker in the image. As seen in figure 6, the darker As atoms do not occur randomly, but rather, they exist in dark bands three to four lattice spacings in width (about 2 nm) extending in the [112] and [112] directions. These bands are indicative of regions of high Al content, formed during growth. The regions appear to nucleate on the left side of the 10 nm layer, and grow through the layer (superlattice growth direction is left to right in figure 6).

Clustering effects similar to that discussed above are expected to occur in many alloy systems. Crosssectional STM results have recently been reported for the InGaAs system, as shown in figure 7 [27]. In the In_{0.2}Ga_{0.8}As layers, InAs is found to cluster preferentially along the growth direction, with each cluster containing two to three indium atoms. A few of the InAs clusters are indicated by arrows in figure 7. This indium segregation was observed to induce an asymmetrical interface broadening.

4. Interface roughness

Roughness of interfaces in semiconductor superlattices has significant consequences in device operation. Electron and hole mobility can be adversely affected, and carrier lifetime may be influenced by defects at interfaces. Intermixing at interfaces, as well as the alloy clustering discussed above, will both contribute to roughness. In addition, atomic steps present on the surface during growth (for example due to islanding) will make a major contribution to the roughness. Interface roughness has been studied by many techniques, ranging from atomic level studies by cross-sectional transmission electron microscopy (TEM) [37], to photoluminescence (PL) studies which probe length scales greater than 10-20 nm [38]. Nevertheless, the spectrum of interface roughness obtained from such studies is still only semiquantitative [39]. Cross-sectional STM provides the opportunity to obtain a more quantitative spectrum of interface roughness, over the length scale 1-100 nm.

As mentioned above, clustering in alloys is intrinsically linked to interface roughness, and this may lead to complications in comparing roughness determined by different techniques. Such complications are avoided in studies of superlattices made from binary materials. There, differing band energies in the layers lead to strong contrast between layers in STM images.



Figure 7. Two 150 × 120 Å² sTM images showing atomic scale details of InGaAs/GaAs heterostructures. The [001] growth direction is indicated. The images were acquired with a tunnelling current of 0.5 nA at a sample bias of +2.0 V. A few InAs clusters are indicated by arrows. (From [27].)

and interface positions can be easily defined simply as the midpoint in the transition between observed layers. An example of this type of imaging is given in figure 8, where we show data from an InAs/GaSb superlattice with nominal layer thicknesses of 4.2 nm InAs and 2.4 nm GaSb [28]. For filled state images such as this, the GaSb layers are bright and InAs layers dark. Faint fringes, with spacing of 6.0 Å (two bilayers), arise from the atomic planes in the superlattice. The interface between InAs and GaSb layers can be more clearly defined by expanding the grey scale of the image and taking a derivative in the horizontal direction, as shown in figure 8(b). Interface roughness, with step heights of 3-6 Å, is clearly visible there. The interfaces of GaSb grown on InAs are seen to have relatively long flat sections, interrupted by steps separated by about 50 A. Alternatively, interfaces of InAs grown on GaAs are considerably rougher, with average step spacing of 10–20 Å.

From interface profiles of the type shown in figure 8(b), a quantitative spectrum of interface roughness can be obtained. This is shown in figure 8(c) for the InAs/GaSb system, with separate results given for



Figure 8. (a) Constant-current sTM image of InAs/GaSb superlattice, consisting of 42 Å thick InAs and 24 Å thick GaSb layers. The image was acquired at a sample voltage of -1.5 V. The [001] growth direction is indicated. The grey scale range is 2.0 A. (b) Derivative of (a). (c) Interface roughness spectra, computed on the 400 Å long interfaces of (b), using seven interfaces of each type and averaging the results. The data from each interface type are fit to a Lorentzian form, yielding results shown for the roughness amplitudes (Δ) and correlation lengths (Λ). (From [28].)

interfaces of InAs grown on GaSb compared to GaSb on InAs. The spectra are fit to a suitable functional form in order to extract measures of the roughness amplitude Δ and correlation length Λ . A Lorentzian form is found to provide a good description of the data, yielding

roughness parameters as shown in figure 8(c). The roughness amplitudes for the two types of interfaces are comparable, but the correlations lengths for InAs grown on GaSb are consistently two to three times less than for GaSb on InAs, thus demonstrating that the former are rougher. This asymmetry between the types of interfaces is also seen in STM voltage-dependent imaging and spatially resolved spectroscopy measurements. The asymmetry is attributed to the lower surface free energy of Sb compared with As, producing exchange of Sb and As when InAs is grown on GaSb, but not for growth of GaSb on InAs.

Interface asymmetry such as that discussed above has been proposed in many systems, and directly observed in a few. Cross-sectional STM observations of interface asymmetry have also been reported for $Al_xGa_{1-x}As/GaAs$ heterojunctions [25], and for InAs/Ga_{1-x}In_xSb superlattices [34].

5. Band offsets

A most important property of semiconductor superlattices is the offset between the positions of band extrema between adjacent layers. These band offsets determine the operating characteristics of devices fabricated from the layered systems, and adjustment of the offset through material composition allows flexibility in the device characteristics. Determination of band offsets from first principles theory has been difficult, and all practical determinations of the offset are based on some type of optical or electrical measurement. The band offsets are usually not well known in new materials systems, with the confidence of their determination increasing as a system is studied by more and more techniques. The spectroscopic capability of the STM offers a promising tool for determination of band offsets in layered structures. Accuracy of such determination would probably not exceed 0.05 eV in most cases due to limitations such as tip-induced band bending, although a reliable estimate even with this uncertainty is valuable for systems in which no other measurements exist.

Spectroscopic measurements aimed at determining the band offset in $Al_xGa_{1-x}As/GaAs$ have been reported by Salemink and co-workers [21]. Currentvoltage (I-V) characteristics were acquired with spatial resolution of 1.7 nm across Al_xGa_{1-x}As/GaAs interfaces. Representative curves are shown in figure 9, with their spatial location relative to the interface (transition region) indicated. On the GaAs material these curves display a bandgap of approximately 1.5 eV and onset of the valence and conduction bands (VB and CB respectively). For the highly doped p-type GaAs, the Fermi level $(E_F, V_{\text{sample}} = 0)$ is close to the VB edge. The transition across the $Al_x Ga_{1-x} As$ is indicated by the drop of the observed VB edge energy by about 0.30 eV, which provides a lowest order determination of the VB offset in this system. However, it was argued that substantial correction to this value was required to account for the effects of tip-induced band bending (as described



Figure 9. Set of I-V characteristics taken across an $Al_x Ga_{1-x} As/GaAs$ interface. Separation between sampling positions is three unit cells or 1.7 nm. The electronic interface is observed in the spectroscopy by the change in the valence edge energy. (From [21].)

in section 2), which shifts the VB onset in $Al_xGa_{1-x}As$ compared to GaAs by 0.15 eV due to the lower doping level in the $Al_xGa_{1-x}As$. With this correction, the VB offset was found to be about 0.15 eV[†].

Although the quality of the data in figure 9 is high (especially considering the difficulty of the experiment), it should be noted that the direct comparison of I-Vcurves, on a linear scale, exacerbates the tip-induced band bending effects. Better results can be obtained using high-dynamic-range acquisition techniques and/or This latter course was modified analysis methods. used by Shih and co-workers in their observations on sulphur-passivated $Al_xGa_{1-x}As/GaAs$ superlattices [25]. Figure 10 shows an STM image of their sample, prepared by cleaving ex situ and dipping the sample in ammonium This procedure passivates the surface by sulphide. coating it with a layer of sulphur. An important property of such passivated surfaces is that some residual Fermi level pinning does occur on the surface, which is actually useful in screening the electric field from the tip and thus reducing tip-induced band bending effects. The samples were then introduced into the STM chamber through a load lock, and studied in UHV. In this image, the Al_{0.3}Ga_{0.7}As layer appears dark and the GaAs layers light, with a topographic contrast between the two of about 7 Å, as shown in the lower part of figure 10. Electronic effects will, of course, make a significant contribution to this contrast, but such a large topographic difference probably implies some etching due to the passivating procedure.

Band offsets were measured for the system shown in figure 10 by measuring I-V curves with spatial resolution of 0.6 nm across the superlattice, as shown in figure 11. The data were analysed by computing $d(\ln |I|)/dV$ which, to lowest order, diverges at the band edge V_0 with a $1/(V-V_0)$ dependence. VB edges determined from this technique were found to

[†] Deducing the band offset is actually more complicated, due to band bending in the superlattice resulting from charge transfer between layers, as discussed in [21].



Figure 10. A 700 × 500 nm sTM image of Al_{0.3}Ga_{0.7}As/GaAs heterojunctions acquired with sample bias of -2.35 V and tunnel current of 0.3 nA. The upper part is the structure of the heterojunctions grown by MBE and the lower part is a line cut across the image (position indicated by the broken line). (From [25].)

be offset by 0.17 ± 0.04 eV between Al_{0.3}Ga_{0.7}As and GaAs. Furthermore, the transition width from one material to the other was found to be significantly larger for the GaAs on Al_{0.3}Ga_{0.7}As interface compared to Al_{0.3}Ga_{0.7}As on GaAs. It was thus concluded that the former (the so-called 'inverted' interface) was rougher, consistent with previously held assumptions regarding properties for these two interfaces.

6. Band structure and quantum well spectroscopy

The STM offers a unique ability to probe filled and empty states a few eV on either side of the Fermi level. This is useful not only in probing interfaces and quantum wells, but also for studying bulk spectroscopy of MBE grown layers. In figure 12 we show spectroscopy of GaAs and Al_{0.3}Ga_{0.7}As, obtained from the sulphur-passivated superlattices shown in figure 10 [25]. In the GaAs spectrum curve, figure 12(b), one can clearly identify three band thresholds which appear as kinks in the I-V curve and in the plot of the numerical derivative (dI/dV) shown in the inset. On the other hand, for $Al_xGa_{1-x}As$, figure 12(c), only two band thresholds are seen. These data were fit to yield energies of the Γ , L and X thresholds of each material, yielding values of 0.65, 0.91 and 1.11 eV respectively for GaAs, and 0.87, 0.98 and 1.07 eV for $Al_xGa_{1-x}As$ (with the latter two values being approximate since the thresholds are



Figure 11. (*a*) Two representative spectra acquired at GaAs and $Al_xGa_{1-x}As$ regions respectively. (*b*) The upper part is a 48 × 21 pixel sTM image in which tunnelling I-V spectra were taken at each pixel in the image. The lower part is the plot of normalized conductivity $d(\ln |I|)/dV$ (derived from tunnelling I-V spectra) versus position at a negative sample bias (-1.59 V). Each data point in this plot represents the average result from the I-V spectra averaged along the vertical direction in the image. (From [25].)

overlapping). The CB offset value was determined to be 0.22 ± 0.04 eV.

In the above example, sulphur passivation of the surface eliminated any trace of the intrinsic surface states of the (110)-cleaved surface. This is in contrast to the results for cleaved GaAs, figure 4, and results shown in figure 13 for GaSb and InAs [28]. Spectra acquired from bulk materials are shown in figures 13(a) and (b). Spectral features are indicated in figure 13, where the energetic positions are determined using peak locations for surface states, and assuming linear onsets for the bulk bands, with a precision of ± 0.03 eV. Bulk bandgaps are marked by dotted lines, with observed values of 0.78 eV for GaAs (compared with known value of 0.72 eV), and 0.35 eV for InAs (compared with known value of 0.36 eV). An additional onset is seen in the conduction band of InAs, and is attributed to the L-valley conduction band, with observed value of 1.18 eV above the CB minimum (compared with known value of 1.08 eV). Surface states appear in the spectra as small peaks, as marked by thin vertical lines in figure 13, and good



Figure 12. (a) The multiple-valley band energy diagrams of the conduction bands of GaAs and $Al_{0.3}Ga_{0.7}As$. (*b*), (*c*) Tunnelling *I*–*V* spectra with sample biased positively (tunnelling into empty states) in GaAs and $Al_{0.3}Ga_{0.7}As$ regions respectively. The vertical scale for $Al_{0.3}Ga_{0.7}As$ has been scaled down by a factor of 0.4. The dots are experimental data and the full curves are fitted spectra. Insets in (*b*) and (*c*) correspond to the numerical derivative, dI/dV, of the *I*–*V* spectra. (From [25].)



Figure 13. Typical tunnelling spectra, acquired from (a) bulk GaSb, (b) bulk inAs, (c) GaSb superlattice layer and (d) inAs superlattice layer. Apparent bandgaps are indicated by dotted lines, surface states by tic marks and L-valley conduction band onsets by upward-pointing arrows. Downward-pointing arrows indicate subband onset energies in panel (d). (From [28].)

agreement is found in their observed locations compared to inverse photoemission results [17].

Spectroscopy has also been performed on GaSb and InAs quantum wells, of the type shown in figure 8, and results are given in figures 13(c) and (d) [28].

Compared to the bulk spectra, some new features are apparent. First, significant conductance is observed within the apparent bandgap regions. Based on the intensity and spatial dependence of this feature, it is interpreted as arising from electron (hole) states tailing out from neighbouring InAs (GaSb) layers. Second, the apparent bandgaps are found to be slightly larger for the superlattice compared with the bulk, with observed gaps of 0.82 and 0.62 eV for the GaSb and InAs layers respectively. The significantly larger gap for InAs is attributed to confinement effects in the quantum well (this effect is smaller for GaSb due to the much larger heavy-hole mass); subtracting the known InAs gap yields an energy for the first electron subband of 0.26 eV. The third feature seen in the superlattice spectrum is an additional onset at 0.51 eV, which is attributed to the second electron subband. Relative to the observed InAs valence band edge, it is located at 1.18 eV, and subtracting the InAs bulk gap yields an energy of 0.82 eV. These subband energies (0.26 and 0.82 eV) are in reasonable agreement with theoretical estimates based on an eight-band tight binding model [28] of 0.21 and 0.77 eV, thus confirming their identification.

The above spectroscopy of InAs/GaSb superlattices has been performed in a spatially resolved mode across the layers [28]. Spectra were acquired each 0.1 nm across the superlattice, and individual spectra acquired at the interfaces could thus be examined. An asymmetry was found in the results for InAs grown on GaSb compared with GaSb on InAs, consistent with the asymmetry in roughness seen in figure 8.

7. Defect studies

In addition to the dopant atoms discussion in section 2, the STM has been applied to the study of other bulk defects. Specifically, GaAs grown at low temperatures (LT) near 200 °C has been studied [29, 30]. The asgrown (unannealed) material is known to contain ar excess arsenic concentration of about 1 at.%, leading to a concentration of point defects (mainly arsenic antisite defects) of about 1×10^{20} cm⁻³. Subsequent annealing causes this excess arsenic to agglomerate and form precipitates. In both the as-grown and the annealed material, the Fermi level is generally found to be pinned near midgap, leading to relatively high resistivities whicl are useful for device applications. For as-grown materia this pinning is attributed to the arsenic-related poin defects, but for annealed material some controvers exists as to the relative role of the arsenic precipitates i the pinning compared with that of residual point defect [40]. STM images and spectra of both the unanneale (LTU) and annealed (LTA) material are presented below

Figure 14 shows STM images of a LTU GaAs laye [29]. These images are acquired with negative sample bias, so that the background atomic corrugation arise from the As sublattice of the GaAs. Numerous defect are visible in the images, and these defects can the classified into several types as labelled in figure 14. The



Figure 14. STM images of the (110)-cleaved surface of unannealed LT GaAs, acquired with 0.1 nA tunnel current and at a sample voltage of -2.0 V. Various point defects can be seen, and they are classified as types A, B, C and D as indicated. (From [29].)

largest apparent defect is type A, and the next largest is type B. Note the presence of two distinct satellite features on the left-hand side of the type-B defects, and these satellites can be faintly seen around the type-A defects as well. Other smaller types of defects are labelled C and D in figure 14, and most unlabelled defects in the images can be seen to fall within one of these four classes. These various types of images are interpreted as all arising from the same type of defect, with the core of the defect being located in differing planes relative to the (110) cleavage plane. Specifically, the image types A, B, C and D are interpreted as arising from arsenic-related detects located zero, one, two or three planes (2.0 Å spacing) below the surface. The core of the defect is identified as being an arsenic antisite (As on a Ga site, As_{Ga}), which is known to be the dominant defect in the material and is consistent with both the structure and spectroscopy of the defects seen in STM. The satellite features seen around the defects are interpreted in terms of tails of the antisite wavefunction.

Spectroscopic results of the LTU GaAs are shown in figure 15, obtained from samples of various doping concentration $(p^{++} = 5 \times 10^{19} \text{ cm}^{-3}, n^+ \text{ and } p^+ =$ 1×10^{19} cm⁻³) [29]. The spectra reveal tunnelling out of valence band states at large negative voltages and into conduction band states at large positive voltages, with the band edges denoted by E_v and E_c respectively. These bands are separated by the bulk bandgap of 1.43 eV. On a region of the LT layer which is not on a point defect, the spectra reveal zero current and conductance within the gap. If the probe tip is positioned on top of a point defect, then the spectra reveal large peaks within the gap region as seen in figure 15. This band of states is attributed to the donor states of the bulk arsenic antisite defect, as shown in the top of figure 15 relative to the band edges of spectrum (a).



Figure 15. Tunnelling spectra acquired from layers of unannealed LT GaAs containing varying amounts of compensating shallow dopants. The valence band maximum (E_V) and conduction band minimum (E_C) are indicated by dotted lines in each spectrum. An intense band of states, arising from arsenic-related defects, appears within the bandgap. The states of a bulk arsenic antisite defect (EL2) are shown in the upper part of the figure, relative to the band edges of spectrum (a). (From [29].)

As the doping is varied from n-type to p-type, the Fermi level moves into this band, indicating that the states are indeed donors. For spectrum (c), in which the Fermi level is roughly in the middle of the deep defect band, a distinct minimum in conductance forms at the Fermi level, indicating a gap of about 0.4 eV in the state density. This conductance minimum is interpreted in terms of Coulomb interactions, both on-site and off-site, at the defects.

Figure 16 shows STM images obtained from the LTA GaAs annealed at 600 °C, showing topography and conductance in (a) and (b) respectively [30]. As marked in the conductance image, the LTA layer extends over most of the image, with the neighbouring p layers seen at the right- and left-hand sides of the image. Two steps occur on the cleavage face in the LTA layer, as marked by the arrows at the top of figure 16(a), and these steps lead to some local pinning of the surface Fermi level as seen by the dark lines occurring at the same spatial location in figure 16(b). Small protrusions can be seen in the LTA layer, appearing as white circular areas in figure 16(a). These protrusions have typical diameter of about 50 Å and height of 15 Å (the observed diameter is sometimes) larger due to tip convolution effects; the 50 Å value is derived from measurements with relatively sharp probe tips). Such protrusions are never seen on n- or p-type material grown at temperatures of 350 °C or higher, and thus they are identified as the arsenic precipitates which are known to occur in this material.

Figure 17 shows spectroscopy results obtained from the LTA layer [30]. Spectra were acquired on the precipitates themselves, and on regions of the bare GaAs in between the precipitates. On the bare GaAs, a



Figure 16. STM image of a cleaved GaAs structure, showing (*a*) topography and (*b*) conductance, acquired at a sample voltage of -2.5 V. The grey scale range in (*a*) is 8 Å. As indicated in (*b*), the structure contains an LTA n-type layer, surrounded by p-type layers grown at higher temperature. The sample was annealed at 600 °C. Two steps occur in the LTA layer, as marked by arrows in (*a*). (From [30].)

bandgap is seen extending from about -0.65 to +0.8 eV, indicating a pinned Fermi level at $E_F = E_V + 0.65$ eV. No states are visible in the gap for the GaAs spectra. On the precipitates a bandgap is observed at about the same location, but now tails of states are observed extending into the gap. These gap states are most pronounced on the conduction band side of the spectrum, but can also be seen on the valence band side. Since these gap states are only observed on the precipitates, and are the only source of gap states anywhere within the LTA layer, the precipitates are identified as being responsible for the Fermi level pinning observed throughout this n-type LTA layer.

8. Other studies

We briefly mention here some other cross-sectional STM studies which have not been covered in this review. Two such studies have already been mentioned in section 1, namely studied of Si/SGe superlattices [31-33], and ex situ studies of GaAs structures [16]. In both of these cases, atomic resolution imaging has not been achieved due to residual defects present from the preparation procedure, but the works nonetheless are important advances in terms of STM applications. Another type of study which has not been discussed here involves optical detection of luminescence excited by tunnelling electrons (or holes) from the STM tip. Such work has been reported by Alvarado and co-workers on $Al_xGa_{1-x}As/GaAs$ superlattices [35, 36]. Luminescence energies indicative of quantum well subbands have been detected, and band offset energies have been deduced. This field appears to be a promising one for future work.



Figure 17. STM spectra acquired from the LTA n-type layer. Spectra are shown acquired on the arsenic precipitates (full curve) and on regions of bare GaAs in between the precipitates (broken curve). The valence and conduction band edges are marked by E_V and E_C respectively. (From [30].)

9. Summary

In this paper we have reviewed cross-sectional STM work performed on cleaved III-V semiconductor structures, providing illustrative examples of various physical properties which can be probed. Within the area of doping profiles and pn junctions, we find that the STM provides a resolution of about 1 nm in determining doping concentrations in the range 10^{18} - 10^{19} cm⁻³. Doping concentrations one or two orders of magnitude lower than this can potentially be determined, once the effects of tip-induced band bending are more quantitatively understood. For alloy fluctuations and clustering, the STM provides a new and powerful probe of the local atomic composition, and more studies along these lines will probably yield a new physical understanding of the clustering processes. Similarly, interface roughness can be probed with quantitative accuracy better than that available by other techniques. Spatially resolved spectroscopic measurements can be used to determined band offsets with an accuracy of about 50 meV, which is particularly useful for new materials systems. Spectroscopy of bulk materials yields threshold energies for valence and conduction bands, and subband energies can be determined in quantum wells. Local variation of these quantities may prove important in our understanding of the physics of small structures. Finally, for the case of defects in the materials, the STM provides the opportunity for determining both the structural and electronic properties of the defects, at least for cases where a sufficiently high defect concentration $(\gtrsim 10^{18} \text{ cm}^{-3})$ is present.

The above-mentioned applications of cross-sectional STM, powerful as they are, have only been applied to a narrow range of materials. Specifically, epitaxial layered structures composed of III–V semiconductors, which are easily prepared by cleavage along a (110) plane. Atomically flat cleavage faces are routinly obtained, this (110) surface is unreconstructed, and it has dangling bond states which do *not* appear in the bandgap. Thus it

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is ideal for cross-sectional studies. Similarly favourable preparation is expected for II-VI semiconductors. For highly strained systems, or non-epitaxial structures, the presence of the strain and/or dislocations may adversely affect the cleavage quality. Even worse, for the case of Si cleavage surfaces [(111) or (110)], dangling bond states completely dominate the surface electronic Passivation of these states is necessary, spectrum. and even the best passivation techniques currently available leave a rather large number of residual surface defects which interfere with the STM studies. More work is required in the preparation of such materials, to enable atomic resolution STM studies. For nonsemiconductor materials such as metallic superlattices preparation procedures to permit cross-sectional STM studies are unknown at present.

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