Direct Mapping of Electronic Structure Across Al$_{0.3}$Ga$_{0.7}$As/GaAs Heterojunctions: Band Offsets, Asymmetrical Transition Widths, and Multiple-Valley Band Structures

S. Gwo, K.-J. Chao, and C. K. Shih
Department of Physics, University of Texas, Austin, Texas 78712

K. Sadra and B. G. Streetman
Microelectronics Research Center and Department of Electrical and Computer Engineering, University of Texas, Austin, Texas 78712
(Received 28 April 1993)

By using the prototypical Al$_{0.3}$Ga$_{0.7}$As/GaAs system, we demonstrate the unique capability of scanning tunneling microscopy to directly map out detailed electronic structure across heterojunctions. Three novel applications are reported: (1) precise determination of band offsets, (2) measurement of asymmetrical electronic transition widths between the normal and inverted interfaces, and (3) mapping of multiple-valley band structures. Important implications of these results are discussed.

PACS numbers: 73.61.Ey, 61.16.Ch, 81.60.Cp

Semiconductor heterojunctions have played very critical roles in the development of modern electronic and photonic devices. For years there have been intensive research activities aimed at a full understanding of the electronic properties of semiconductor heterostructures. Compared with conventional techniques such as photoluminescence, photoemission, and C-V measurements, scanning tunneling microscopy and/or spectroscopy (STM/S) has unprecedented resolution for direct mapping of the spatial variation of electronic properties. Thus, it is an ideal tool for studying heterostructures.

Such a promising potential has motivated many researchers [1-9] to develop cross-sectional STM to study semiconductor heterostructures. In terms of the atomic registry, there has been significant progress [1,2]. However, the most unique feature of this technique, the direct mapping of electronic structure across heterojunctions, has not been fully achieved. The tip-induced band bending effect was realized to be a major problem [2]. In the case of homogeneous GaAs, this problem can be overcome by using highly doped samples where the high carrier density screens the field within a short length [10]. However, in heterojunctions (or pn junctions), right at the area of interest there exists a depletion region which inevitably suffers a severe tip-induced band bending effect. Thus, if the full potential of STM to directly map out electronic structure across heterojunctions is to be realized, the tip-induced band bending problem needs to be solved. We achieve this by passivating the cleaved surface with sulfide solutions [11-15] which we find to produce a uniformly pinned Fermi level. Since the extrinsic surface states which pin the Fermi level also screen out the electrical field, the tip-induced band bending is avoided. A similar situation has been observed by Feenstra and co-workers [4,5] on a highly stepped surface whose Fermi level is also strongly pinned.

With the problem of tip-induced band bending solved, we have been able to demonstrate this particularly important application of cross-sectional STM: the direct mapping of electronic structure across heterojunctions with nanometer resolution. We report three important results: (1) precise determination of band offsets, (2) measurement of asymmetrical electronic transition widths between the normal and inverted interfaces, and (3) detailed mapping of multiple-valley conduction band structures for GaAs and Al$_{0.3}$Ga$_{0.7}$As.

Our experiments were performed in a UHV-STM system (base pressure < 7×10$^{-11}$ Torr) equipped with a dual-axis sample translation stage and a sample lock. The Al$_{0.3}$Ga$_{0.7}$As/GaAs heterojunctions were grown by molecular-beam epilaxy at 620°C under As stable conditions. Doping levels in our samples are 2×10$^{18}$ cm$^{-3}$ both for $p$ type (Be dopant) and $n$ type (Si dopant). Two Ga sources were employed to allow equal doping in GaAs and (AlGa)As layers. Samples were cleaved ex situ and passivated in an ammonium sulfide [NH$_4$]$_2$S solution at room temperature for 5-20 min. After rinsing in deionized water and blowing dry with nitrogen gas, the samples were immediately transferred into the UHV chamber through a load lock for STM measurements. Tungsten tips were cleaned in situ using the field emission method on separate clean substrates.

Figure 1 shows a filled-state STM image of the sulfide-passivated sample with the corresponding growth structure displayed above it. The GaAs buffer layer shown in the image allows an unambiguous assignment of the GaAs and (AlGa)As regions. From the line cut shown below, one finds that (AlGa)As regions appear deeper than GaAs regions by about 5 Å. We believe the generally deeper appearance of the (AlGa)As regions in our work is primarily an electronic effect since this apparent height difference does not depend on the duration of time that the sample is passivated inside the sulfide solution. An atomic force microscopy study may provide more conclusive evidence regarding the true topographic height difference. The inverse decay constant $\kappa$ measured on such a sulfide-passivated surface shows a typical value of 0.95 ± 0.2 Å$^{-1}$, suggesting a good vacuum tunneling
condition. Although we have not observed an atomically resolved image on the passivated surface, the measured rms roughness in the substrate region is less than 0.5 Å, indicating an atomically flat surface.

Typically, tunneling spectra were acquired on 64×64 pixel images where I-V tunneling spectra were recorded at each pixel by interrupting the STM feedback. Shown in Fig. 2(a) are two representative spectra acquired at GaAs and (AlGa)As regions. These two spectra show gap values of 1.4 ± 0.1 and 1.8 ± 0.1 V, consistent with the band gaps of GaAs and (AlGa)As, respectively. Shown in Fig. 2(b) is a 48×21 pixel image which covers a region of p-Al_{0.3}Ga_{0.7}As/p-GaAs/p-Al_{0.3}Ga_{0.7}As. In principle most of the important spectroscopic information is contained in those I-V spectra but extraction of useful information is nontrivial. For example, to determine the band edge, one method used by others has been to fit the I-V curve near the threshold [16]. While such a fitting process is also used, the majority of our data are analyzed by using a normalized conductivity d(ln[I])/dV method which provides a “parameter free” procedure to extract important information. A similar method has been used by Feenstra et al. [4,5] to reveal GaAs pn junctions. The basic principle for the conductivity method is that if the tunneling current has a power law dependence of the form $I \sim (V - V_0)^a$ near the band threshold where $V_0$ is the threshold, then $d(ln[I])/dV = a/(V - V_0)$, showing a $1/(V - V_0)$ dependence [4,5]. As a result, the closer to the band edge, the larger this normalized conductivity is.

Indeed, as shown in Fig. 2(b), a larger value of $d(ln[I])/dV$ is found in the (AlGa)As region, indicating the existence of a valence band offset (VBO) [17].

For the filled states, the voltage dependent behavior of $d(ln[I])/dV$ shows nearly ideal $1/(V - V_0)$ behavior with the power law factor $a$ varying from 1.5 to 2.0. Consistent contrast of $d(ln[I])/dV$ vs x is also observed over a large range (~1 V) of sample bias. The spatial dependence of the valence band maximum (VBM) positions can be estimated directly from the normalized conductivity plot since $V_0 = V - a[d(ln[I])/dV]^{-1}$. Shown in Fig. 3(a) is a VBM vs x plot obtained from the $d(ln[I])/dV$ plot shown in Fig. 2 by using $a = 1.5$. The VBO can be deduced from this plot to be 0.17 ± 0.04 eV. VBM vs x plots deduced from $d(ln[I])/dV$ at different biases show nearly identical band offsets except that their absolute energy positions may vary. A more accurate determination of absolute VBM positions can be obtained from a fitting procedure of the I-V curves, resulting in $-0.78 \pm 0.03$ eV for GaAs and $-0.95 \pm 0.03$ eV for Al_{0.3}Ga_{0.7}As relative to the surface Fermi level. The resulting VBO is identical to that determined by the conductivity plot. Although the absolute band edge positions are determined more precisely using the I-V fitting procedure, we emphasize that the $d(ln[I])/dV$ plot offers a much more effective method to show the spatial variation of electron-
FIG. 3. (a) The positions of valence band edges (referenced to the Fermi level) across the Al0.5Ga0.5As/GaAs heterojunctions determined by the $d\ln|I|/dV$ vs $x$ plot at a sample bias of $-1.59 \text{ V}$. The curve has been offset upward by 0.15 eV so that the absolute position of the VBM agrees with that determined by the $I$-$V$ fitting procedure. (b) A histogram of transition widths for normal (full bar) and inverted (open bar) interfaces.

FIG. 4. (a) The multiple-valley band energy diagrams of the conduction bands of GaAs and Al0.5Ga0.5As. (b),(c) The tunneling $I$-$V$ spectra with the sample biased positively (tunneling into empty states) in GaAs and Al0.5Ga0.5As regions, respectively. The vertical scale for Al0.5Ga0.5As has been scaled down by a factor of 0.4. The dots are experimental data and the solid curves are fitted spectra. Inset in (b) and (c) correspond to the numerical derivative, $dl/dV$, of the $I$-$V$ spectra.

ic structures since it is parameter free and the exponential dependence of tip-sample distance is removed.

From Fig. 3(a) one can also see that the surface Fermi level is pinned uniformly across the heterojunctions. It appears that the pinning positions of sulfide-passivated GaAs and Al0.5Ga0.5As are identical, namely, the difference in their pinning position relative to the VBM equals the VBO. However, we should point out the possibility that the pinning positions of isolated GaAs and AlGaAs may differ from the pinning position described here. Since the nature of Fermi level pinning is not of primary concern here, the detailed discussion will be described elsewhere. We emphasize that the pinning of surface Fermi level has the advantage of minimizing the tip-induced band bending effect, and the most important properties of heterojunction, such as band discontinuities, are not affected by the pinning.

The transition width of the electronic interface can also be determined from this VBM plot or the $d\ln|I|/dV$ vs $x$ plot. We determine the transition width ($\lambda_t$) by fitting this VBM vs $x$ plot with a step function convoluted with a Gaussian function. The FWHM of the Gaussian function is assigned to be $\lambda_t$. One can observe that the transition width at the right hand side (RHS) interface is wider than that at the left hand side (LHS) interface. The RHS interface corresponds to the so-called “inverted interface” [GaAs on the growth front of (AlGa)As] while the LHS interface corresponds to the so-called “normal interface” [18]. The histogram shown in Fig. 3(b) represents the transition widths $\lambda_t$ measured at different locations along [110] with the same tip. As one can see, the average values of $\lambda_t$ and its statistical deviation, $\sigma_t$, at the inverted interface are larger than those at the normal interface, implying a greater interfacial roughness [19]. One can rule out that the observed asymmetry is a tip-shape effect since that would not result in a larger $\sigma_t$ at the inverted interface. The issue of interfacial roughness in normal vs inverted interfaces has been an important topic because it crucially affects the device characteristics when the device dimensions become very small. While the metallurgical aspect of interfacial roughness has been investigated by transmission electron microscopy (TEM) [20], we reveal, for the first time, the consequence of such roughness on the electronic transition width in real space.

As stated earlier, $d\ln|I|/dV$ shows nearly ideal $1/(V-V_0)$ behavior. This is due to the fact that the heavy hole band makes a dominant contribution to the density of states. On the other hand, the conduction band structure indicates many valleys as shown in Fig. 4(a). In this figure, we have aligned the conduction bands of the Al0.5Ga0.5As and GaAs according to the determined conduction band offset (CBO). The relative band edge locations between Al0.5Ga0.5As and GaAs depend on which valley is being considered: at $\Gamma$, one has a positive band offset of about 0.2 eV; at $L$, the band offset is smaller; and at $X$, the Al0.5Ga0.5As band even lies below the GaAs band. This complicated conduction band structure gives rise to a nontrivial $d\ln|I|/dV$ behavior.
The multiple-valley conduction band structure is clearly observable in our I-V spectra. Representative spectra acquired on GaAs and Al_{0.3}Ga_{0.7}As regions are shown in Figs. 4(b) and 4(c), respectively. These two spectra are each averaged over about 100 individual I-V curves acquired in a region of 40 Å (along x) by 1000 Å (along y) to obtain a better signal to noise ratio. In the GaAs I-V spectrum, 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_{0.3}Ga_{0.7}As, only two band thresholds instead of three are clearly seen (better observed in the dI/dV plot).

The energy positions of the thresholds can be determined more precisely by employing a fitting procedure similar to those used in ballistic electron emission microscopy (BEEM) [21]. The power law parameter used here, however, is different from that used in BEEM because the kx conservation does not exist in STM. Since the bulk density of states has a square root energy dependence, we use a power law parameter of 1.5. This fitting procedure gives the following thresholds for GaAs: 0.65 eV for Γ, 0.91 eV for L, and 1.11 eV for X. It also gives the following thresholds for Al_{0.3}Ga_{0.7}As: 0.87 eV for Γ, 0.98 eV for L, and 1.07 eV for X. For Al_{0.3}Ga_{0.7}As, since the energy separation between the L and X thresholds is very small (ranging from 25 to 50 meV according to Ref. [22]), only two thresholds are clearly identifiable in our data due to thermal broadening of the tip Fermi edge. Therefore, the deduced values for the L and X thresholds are only approximate. The CBO value is determined to be 0.22 ± 0.04 eV.

The experimentally determined values of the multiple band thresholds show excellent agreement with the theoretical values [22] for GaAs and reasonable agreement for Al_{0.3}Ga_{0.7}As. For GaAs, these values are also consistent with those obtained using BEEM [21]. For tunneling spectra acquired on a UHV-cleaved GaAs surface, we do not observe the multiple band thresholds. We attribute this difference to the removal of intrinsic surface states on the cleaved (110) surface by the sulfide passivation.

In summary, by using sulfide passivation to solve the tip-induced band bending effect, we have achieved direct and detailed mapping of electronic structure across (AlGa)As/GaAs heterojunctions. While the determined band offset values are consistent with those obtained by conventional methods, important applications of this approach should be found in other systems where band offset values are still not well characterized. The observation of asymmetrical electronic transition widths at the normal and inverted interfaces demonstrates the unique ability of STM to determine the local abruptness of the electronic interface. We also show that the multiple-valley band structure in these compounds can be locally resolved. This ability can be extended to probe the strain-induced band splitting in strained-layer systems. All these demonstrated capabilities show great promise for advancing our understanding of the local electronic structure of semiconductor heterostructures.

This work was supported by the Texas Advanced Research Program, the Joint Services Electronics Program (No. AFOSR F49620-92-C-0027), and the Science and Technology Center Program of NSF (No. CHE-8920120).

[17] We typically average the tunneling spectra along the [110] direction over about 5–20 nm before performing the logarithmic derivative.
[19] The so-called “interfacial roughness” is a matter of definition. The composition and band structure of an alloy is not well defined unless an average is performed over a certain length scale. In Ref. [18], a length scale of 2–4 nm was used. In the TEM studies (see Ref. [20]), the length scale corresponds to the thickness of the sample (~10 nm). In our case, since we average I-V spectra along [110] over about 5–20 nm before deducing d(ln|I|)/dV, this is the length scale over which our alloy composition is defined.
FIG. 1. A 7000 Å×5000 Å STM image of Al\textsubscript{0.3}Ga\textsubscript{0.7}As/GaAs heterojunctions acquired with a sample bias of −2.35 V and a tunneling current of 0.3 nA. The upper part is the structure of Al\textsubscript{0.3}Ga\textsubscript{0.7}As/GaAs heterojunctions grown by MBE and the lower part is a line cut across the image (position indicated by the dashed line).
FIG. 2. (a) Two representative spectra acquired at GaAs and AlGaAs regions, respectively. (b) The upper part is a 48×21 pixel STM image in which tunneling $I$-$V$ spectra were taken at each pixel in the image. The lower part is the plot of normalized conductivity $\frac{d(\ln|I|)}{dV}$ (derived from tunneling $I$-$V$ spectra) vs position at a negative sample bias (−1.59 V). Each data point in this plot represents the average result from the $I$-$V$ spectra along the $y$ direction.