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The Continuing Drama of the Semiconductor Interface

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The continuing drama of the semiconductor interface

By J. M. Woodall[1], P. D. Kirchner[1], J. L. Freeouf[1], D. T. McInturff[1], M. R. Melloch[2] and F. H. Pollak[3]

[1] *IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598, U.S.A.*

[2] *School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907, U.S.A.*

[3] *Physics Department, Brooklyn College of CUNY, Brooklyn, New York 11210, U.S.A.*

Studies on III–V compound semiconductor surfaces and metal interfaces are discussed. For GaAs and InP surfaces aqueous photowashing or chalcogenide coatings can significantly reduce surface state densities. For metal interfaces experimental conditions have been found which lead to metal work function dominated Schottky barrier heights to GaAs. Finally, using special epilayer samples of GaAs, AlGaAs and InGaAs containing a significant excess of As, more has been learned about the origin of the invariance of the interface Fermi level (pinning) commonly observed at III–V semiconductor interfaces. The excess As can form either a high density of point defects or a dispersion of elemental As clusters depending on the post growth annealing conditions. It has been found that the pinning effects of point defects are qualitatively different from those due to the clusters of elemental As. Specifically, when the excess As is in the form of As precipitates, the As forms a Schottky barrier whose barrier height is well characterized by the parameters of As work function and semiconductor electron affinity.

1. Introduction

The large density of uncontrolled surface states commonly observed at most III–V compound semiconductor oxide interfaces has hampered the development of high performance devices, especially photonic devices. These states, whose origin is still a topic of controversy, tend to 'pin' the location of the Fermi level at various semiconductor interfaces at some characteristic energy. Pinning which occurs at metal–semiconductor interfaces at the same characteristic energy as for oxide interfaces implies a common origin of Fermi level pinning for both oxide and metal interfaces. Pinning adversely affects the performance of both high speed and optoelectronic devices and circuits.

The introduction of the lattice matched AlGaAs–GaAs heterojunction (Rupprecht *et al.* 1967) became the basis of a partial solution to the Fermi level pinning problem for many optoelectronic devices, e.g. light emitting diodes, DH lasers, solar cells, etc., and for some high speed devices, e.g. high electron mobility transistors and heterojunction bipolar transistors (HBT). None the less, the Fermi level pinning problem still hampers the development of other desirable devices such as MOSFETs, the optimization of metal contacts, and the passivation of devices and circuits.

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Despite much effort to understand the electronic properties of metal or oxide interfaces there is still no generally accepted theoretical framework which adequately accounts for the myriad of diverse experimental observations. This is especially true for the technologically important metal–semiconductor interfaces. The problem is that very few interfaces are both planar and atomically abrupt, a condition usually needed for theoretical treatment. In addition the regions bounding the interface are usually chemically and structurally non-uniform. Thus, successful theory has been confined to 'ideal' interfaces, such as the epitaxial, atomically abrupt semiconductor heterojunction.

2. Fermi level pinning

Fermi level pinning is manifest in several ways. The two most notable are (1) the apparent insensitivity of the Schottky barrier height to metal work function (Waldrop 1984), and (2) the large density of interface states seen, for example, in GaAs MOS structures (Wieder 1983). Pinning theory can be classified into two groups, Fermi level pinning as an intrinsic property of the semiconductor related to either bulk or surface band structure (Tersoff 1984; Louie & Cohen 1976), e.g. metal induced gap states (MIGS) or some variant; or Fermi level pinning as an extrinsic property of the semiconductor related to native defects (Spicer *et al.* 1979), disorder (Hasegawa & Sawada 1983), or anion phase work function known as the effective work function (EWF) model (Freeouf & Woodall 1981). The EWF model posits that the interface Fermi level is determined by the work function of a 'dominant' interface phase via the Schottky model. Thus, pinning in the EWF model is only apparent and is due to the uncontrolled presence of elemental anion, e.g. As for GaAs, at the interface. In addition the EWF model and a model by Duke and Mailhiot (Duke & Mailhiot 1985) predict that in the absence of factors which cause extrinsic Fermi level pinning, the Schottky work function limit should be the dominant mechanism for locating the interface Fermi level.

3. Techniques for producing low surface state density

(*a*) *Photowashed* GaAs

In the photowash (PW) method the GaAs surface is illuminated with greater than band gap energy photons at an intensity on the order of 10 W cm^{-2}. The light source is typically either an ELH tungsten halogen 300 W projector bulb or an argon ion laser (488 nm). During the photon illumination the GaAs is mounted on a photoresist type 'spinner' and flushed with deionized water for a period which can be varied from between 10 and 10^3 s. As a result of this treatment it has been previously shown (Kirchner *et al.* 1988) that the GaAs surface is passivated with an oxide layer whose chemistry is predominately Ga_2O_3 with only a trace of either As or As_2O_3, and whose thickness is an increasing function of photowash time. For the case of PW generated oxides of greater than 5 nm thickness, a 'photoactivation' step after PW is necessary to reduce the band bending so that an increased photoluminescence (PL) will be seen (Wilmsen *et al.* 1988). The photoactivation step apparently causes the desorption of a residual charged species which acts as a different pinning site. Evidence for a reduced interface state density includes: increased band edge PL (Offsey *et al.* 1986; Ives *et al.* 1987), a reduced surface recombination velocity (Hasegawa *et al.* 1988; Yablonovitch *et al.* 1987; Beck & Wessel 1987), *C–V* characterization (Offsey *et al.*

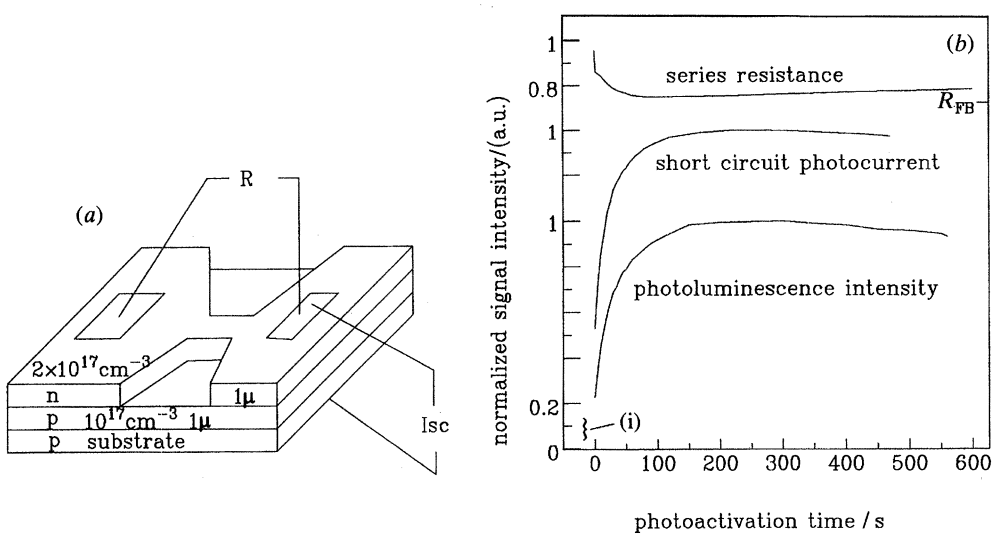

Figure 1. (*b*) Intensity: 0.25 W cm^{-2}, 440 nm excitation; (i) approximately pre-PW PL signal.

1986), and the photoreflectance modulation of the surface electric field (Shen *et al.* 1990).

In spite of the many positive indications that the PW technique leads to GaAs with a low surface state density and hence more nearly flat band, PW experiments by Hasegawa *et al.* (1988) have resulted in surfaces with increased band bending, as indicated by resistance measurements on ungated FET structures which have had the PW treatment. As a result the IBM group performed an experiment using a special structure shown schematically in figure 1. The GaAs structure is basically an n–p photovoltaic device in which PL, the short circuit current, and sheet resistance of the top n-layer can be monitored during the PW treatment. As shown in figure 1, and contrary to the results of Hasegawa *et al.* (1988), there is a *decrease* in sheet resistance after PW. This decrease in sheet resistance correlates with an increase in both the PL and short circuit current and is consistent with the notion of decreased band bending and surface state density. Thus it has been shown that Fermi level pinning is indeed an extrinsic feature of the dielectric–GaAs interface and that a dielectric layer can be formed on GaAs which does not cause pinning.

(*b*) *Chalcogenide passivation techniques*

Shortly after the report of the photowash results a group at Bellcore (Yablonovitch *et al.* 1987) reported an alternative technique for greatly reducing the GaAs surface recombination velocity. In this technique the native oxides are first removed from the GaAs surface. This is followed by spin coating the surface with a film of $Na_2S{\cdot}9H_2O$. Compared with the PW technique the sulphide film has been shown to impact device technology more directly, for example, by improving the gain of HBTs (Sandroff *et al.* 1987). An ammonium sulphide treatment has been shown to both reduce the surface leakage component in p–n junction diodes (Carpenter *et al.* 1988) and to provide a greater range in Schottky barrier heights than for surfaces with native oxide (Carpenter *et al.* 1989). Other tests demonstrating unpinning include PL studies (Skromme *et al.*) and carrier lifetime studies (Yablonovitch *et al.* 1987). The PL studies by the IBM/Colorado State group (Wilmsen *et al.* 1988) reveal that the

behaviour of the PW and sulphide layers are very similar. Chemical studies reveal that the sulphide passivated layers are such that the GaAs surface is either terminated by gallium rich sulphides (Cowans *et al.* 1989; Tiedje *et al.* 1989) or by an arsenic sulphide compound (Sandroff *et al.* 1989). As is the case for the PW treatment, unpinned sulphide treated layers are associated with the removal of the arsenic components in the native oxide before forming the sulphide layer. Recently passivation has been achieved by MBE of GaSe layers on GaAs (Ueno *et al.* 1992). However, as with the PW treatment, this technique along with the other previous sulphide coating techniques do not result in long term passivation stability. More recently there is a report of long term passivation stability of GaS layers on GaAs deposited from a $[(t\text{-Bu})GaS]_4$ source (MacInnes *et al.* 1993).

4. Schottky limit barriers to metal–(100) GaAs interfaces

Recently, the atomic structure of the (100) GaAs (2×4) reconstruction has been determined by scanning tunnelling microscopy (STM) (Pashley *et al.* 1988). The STM images show that the $4\times$ periodicity is due to a regular array of missing arsenic dimers. This structure had been predicted to have a minimum energy compared with other possible configurations (Qian *et al.* 1987). The calculations also predict a forbidden gap of this reconstruction to be larger than that for bulk GaAs, i.e. no mid-gap surface states, and, hence no inherent mid-gap Fermi level pinning. A key to obtaining the STM result was the use of an As capping layer and desorption technique developed by a Rockwell group (Lowalczyk *et al.* 1981) to protect an MBE grown surface during transit to the STM apparatus.

This same technique was used by the Xerox–Wisconsin–IBM group to prepare Schottky limit barriers to GaAs (Vitturo *et al.* 1989). A summary of the results of this work using soft X-ray photoemission spectroscopy (SXPS) is shown in figures 2 and 3. In figure 2 it should be noted that the As capped and desorbed (100) n-type GaAs appears to be flat band before metal deposition, similar to the case for UHV cleaved (110) GaAs. However, the sample is, in fact, not flat band before metalization. It is an artefact of the measurement which is due to a photovoltaic effect (PVE) caused by the photon flux during the SXPS measurement (Hecht 1990). However, after a monolayer thickness is reached the PVE no longer imparts significant error to the measurement. After about one monolayer coverage, the interface Fermi level approaches that expected for the Schottky work function limit, i.e. $\phi_b = \phi_m - \chi$; $\chi = 4.07$ eV (see figure 3). This behaviour is in contrast with the thick limit of metal deposition on (110) GaAs where mid-gap Fermi level pinning is observed (Spicer *et al.* 1979).

There are several important experimental conditions which must be used to obtain these results. First, the GaAs samples must be grown by MBE on nominal (100) substrates. Misoriented samples will have a large density of atomic steps and kink sites which will pin the Fermi level at n-type (100) surfaces (Pashley 1992). Second, the desorption of the As capping layer must be done at temperatures between 400 and 600 °C, the boundary between lack of complete As desorption and the generation of surface Ga droplets. Third, the metal deposition should be done at temperatures below 100 K, preferably about 80 K. Even so it has been found that these results are difficult to reproduce. Subtle differences in the quality of the MBE GaAs layers and sample preparation limit the range in barrier heights which are observed (Raisanen *et al.* 1993).

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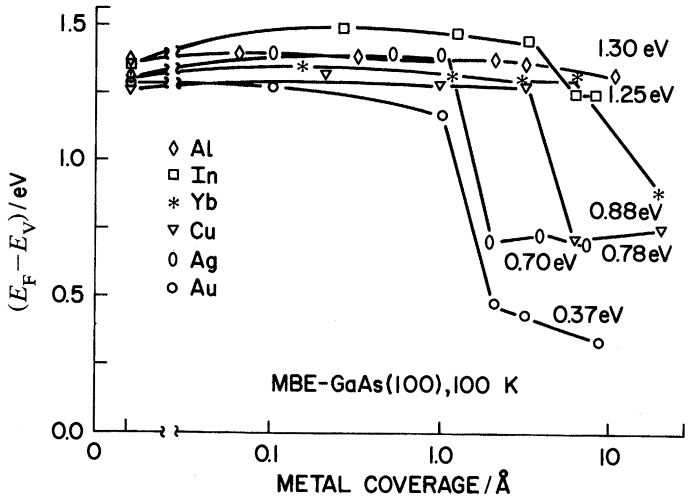

Figure 2

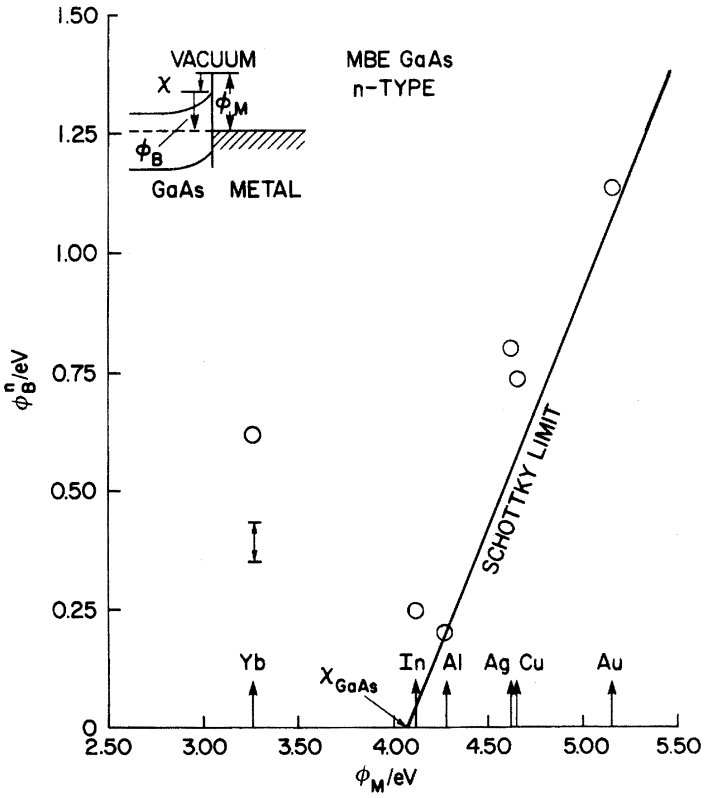

Figure 3

In figure 3 it should be noted that the barrier height for Yb is that expected for the work function of arsenic. This is not surprising since Yb is expected to be highly reactive with GaAs, and thus it is expected that elemental As will be generated at the Yb–GaAs interface. Since figure 3 shows both pinning and Schottky limit behaviour it is very difficult to reconcile this situation with models other than the EWF model.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

It is clear that, for the (100) GaAs used to obtain the data in figures 2 and 3, Fermi level pinning is not an intrinsic phenomenon, thus, MIGS type models do not seem to be appropriate for this case. More recently (Freeouf *et al.* 1990), there was an attempt to explain the lack of dominance of MIGS physics at the metal–(100) GaAs interface shown in figure 3. It is suggested that the (2×4) or other non-metallic surface reconstructions act like an 'insulating' 'I' layer of a MIS like structures which isolates the GaAs bulk from the effects of MIGS. This would 'turn off MIGS' and allow work function physics to dominate as it does for Si MOS structures.

5. III–V materials with excess anion

Having shown that surfaces and metal interfaces of III–V compound semiconductors can be made to be unpinned, the question arises as to the origin of the vast numbers of pinned metal interfaces. This is a difficult question to address. This is because there are at least three models which predict the observed pinning energy using completely different physical arguments. For example, the experimental evidence of the presence of elemental As at pinned GaAs interfaces used for devices does not uniquely resolve this issue in favour of the EWF model where As would act through its work function via the Schottky model. Arsenic, as a metal or semi-metal, could act via MIGS physics. Also, it could be associated with near surface anti-site defects which would pin the Fermi level mid-gap. Thus, determining uniqueness for a pinning model seems futile. On the other hand demonstrating the limits of various models could be useful. For example, figure 3 demonstrates an experimental condition where MIGS physics does not dominate the barrier height. It also demonstrates that for these conditions near surface semiconductor point defects do not dominate the barrier height either. Are there other experimental conditions which exist that might further distinguish the limits of validity of the models? In particular can the direct role of elemental As be distinguished from its possible association with effects due to the presence of anti-site defects? It turns out that such an experiment can be done.

In the past few years it has been discovered that the MBE of GaAs, AlGaAs, and GaInAs at temperatures much lower than those normally used to fabricate high quality layers results in material with a large excess of As over the stoichiometric concentration (Kaminska *et al.* 1989). For GaAs and GaAlAs this lower temperature is between 200 and 300 °C and for GaInAs this temperature is between 125 and 175 °C. In the present work GaAlAs means $Ga_{0.70}Al_{0.30}As$, and GaInAs means $Ga_{0.47}In_{0.53}As$, the composition lattice-matched to InP. In the as-grown condition the excess As concentration can range between 0.5 and 4.0% (Kaminska *et al.* 1989; Kunzel *et al.* 1992). Also, in the as-grown condition, this excess As is in the form of interstitials and anti-site defects, i.e. As on a Ga site. This material has been well characterized by EPR and infra-red absorption measurements (Liliental-Weber *et al.* 1989; Manasreh *et al.* 1990). The EPR result demonstrates an anti-site defect concentration of about 0.1%. Previously, studies on slightly arsenic-rich bulk GaAs crystals revealed that the As anti-site, also referred to as 'EL-2', acts as a deep donor impurity with characteristic ionization state dependent energy levels. These results form the basis of the native defect model for Fermi level pinning at metal–GaAs interfaces (Spicer *et al.* 1979). Therefore, the epilayers with a large As excess should provide more signal to address a possible correlation of anti-site defects with Fermi level pinning. This material is denoted as, for example, LT–GaAs.

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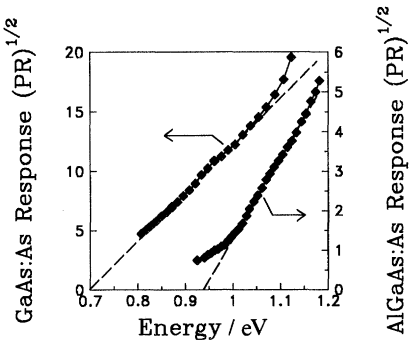

Figure 4

When the as-grown materials are annealed at temperatures used during normal MBE all of the excess As, i.e. the anti-site and interstitial As, coalesces into a dispersion of As precipitates (Melloch *et al.* 1990). These precipitates increase in size, and hence decrease in cluster density, from about 5 nm to about 30 nm as the annealing temperature is increased from 600 to 900 °C. To distinguish the material from the anti-site dominated material it has been given the nomenclature: III–V:V, e.g. GaAs:As, GaAlAs:As, and GaInAs:As. To explain the stability of semi-insulating character of GaAs:As against moderately high levels of n- and p-type doping, it has been argued (Warren *et al.* 1990) that the As precipitates form a buried array of Schottky barriers whose depletion regions overlap, 'pinching off' the bulk of the GaAs in a manner analogous to the gate voltage pinching off the channel of a MESFET. When either the doping level increases or the As particle density decreases, the depletion regions will cease to overlap and the materials will become low resistivity. This behaviour has been observed (Warren *et al.* 1992). By comparing, for example, LT–GaAs with GaAs:As using structures which can determine the pinning energies for each of these materials, it may be possible to distinguish the effects of anti-site defects from those due to elemental As at pinned metal–GaAs interfaces. This has been done using two different structures and two different characterization methods.

(*a*) *Internal photoemission studies*

In the first experiment internal photoemission (IP) is performed on PiN structures of GaAs and AlGaAs in which the 'i' layer is either LT–GaAs or GaAs:As or AlGaAs:As. The assumption in this experiment is that if the As particle in the GaAs:As is a buried Schottky barrier, it will produce a 'normal' Fowler plot, i.e. a linear square root dependence of the photoemission current versus photon energy and whose energy axis intercept is the Schottky barrier height; whereas the point defects in the LT–GaAs are expected to have a different excited carrier supply function, i.e. the structure with 'i' LT–GaAs layer will not produce a normal Fowler plot. The details of the sample structure and sample fabrication has been described previously (McInturff *et al.* 1992). The Fowler plot for PiN structures of p-GaAs–i-GaAs:As–n-GaAs and p-AlGaAs–i-AlGaAs:As–n-AlGaAs is shown in figure 4. Notice the energy axis intercepts of 0.7 eV and 0.93 eV for GaAs:As and AlGaAs respectively. These are thus the Schottky barriers heights of As to GaAs and AlGaAs respectively. Not shown are data for structures with LT–GaAs i layers. This is because there was no measurable signal.

Several conclusions can be drawn from the data in figure 4. First, since the Fowler plot is well behaved for both GaAs and AlGaAs structures, we can conclude that As precipitates in GaAs:As and AlGaAs:As are in fact buried Schottky barriers, similar in behaviour to a planar metal–semiconductor interface. In this regard it should be noted that a well behaved Fowler plot is an accepted technique to determine barrier heights at metal–semiconductor interfaces. The second point is for GaAs:As samples the barrier value of 0.7 eV is the same value previously measured (Rossi *et al.* 1987) for As–GaAs planar interfaces by the current–voltage technique and thus fixes the exact barrier due to As. Third the value of 0.93 for AlGaAs:As samples is the value expected using currently accepted GaAs–AlGaAs band-offset rules and assuming a constant reference energy for As, e.g. the As work function. It is clear the LT–GaAs and GaAs:As are qualitatively different in this experiment. Hence, this experiment supports the EWF model description of Fermi level pinning and in fact defines a new measure for the As work function.

(*b*) *Photoreflectance studies*

In the second experiment photoreflectance (PR) spectroscopy is used to characterize a three layer, doped-I–undoped-I–undoped-II, structure, where layer I is either GaAs or GaInAs grown at normal MBE temperatures and layer II is either LT GaAs or GaAs:As or GaInAs:As.

It has been demonstrated that PR spectra from special sample structures with large, uniform built-in electric fields are extremely useful for evaluating the position of the Fermi level at semiconductor surfaces and interfaces (Yin *et al.* 1992). From the large number of Franz–Keldysh oscillations (FKOs) observed in the PR spectra, it is possible to determine the built-in electric fields (and hence barrier heights) as well as energy gaps in a contactless manner. The key assumption in using this method with the three layer structure is that the Fermi level will be pinned at some characteristic energy in layer II. If so, the electric field will be nearly zero in layer II whereas the electric field will be non-zero and nearly constant in the undoped layer I. A knowledge of the thickness of the undoped layer I and the doping level of doped layer I will allow the determination of the Fermi level in layer II. If layer II is GaAs:As or GaInAs:As and the As precipitates act as buried Schottky barriers with a single pinning position then the Fermi level in II will have the same measured value for structures with either n- or p-doped I layers. If on the other hand layer II is LT–GaAs which has only a deep-donor EL-2 levels, then then Fermi level will be pinned in layer II only for structures in which the doped layer I is p-type.

The apparatus used for PR experiments is reported elsewhere (Glemboki & Shanabrook 1992). As an example of the signal measured in this experiment, the PR spectra for GaInAs grown on InP are displayed in figure 5. The curves for samples A and B are for a three layer structure where doped layer I is p-type GaInAs undoped layer I as GaInAs 100 nm thick and layer II is GaInAs:As 100 nm thick which has been shown by TEM measurements to contain As precipitates. The form of this data is comparable to that previously reported for similar GaAs structures (Warren *et al.* 1992; Shen *et al.* 1992). Sample C is the same as A and B but without the top layer II. For this case the FKO spectra measures the Fermi level pinning position of the free surface of GaInAs. The PR spectra of the three samples are taken at 300 K in the region of the direct energy gap, E_g, of GaInAs. All samples exhibited well pronounced FKOs. For clarity we have plotted the spectra in terms of $E-E_g$, where E is the photon energy. The position of E_g was determined by the three point method

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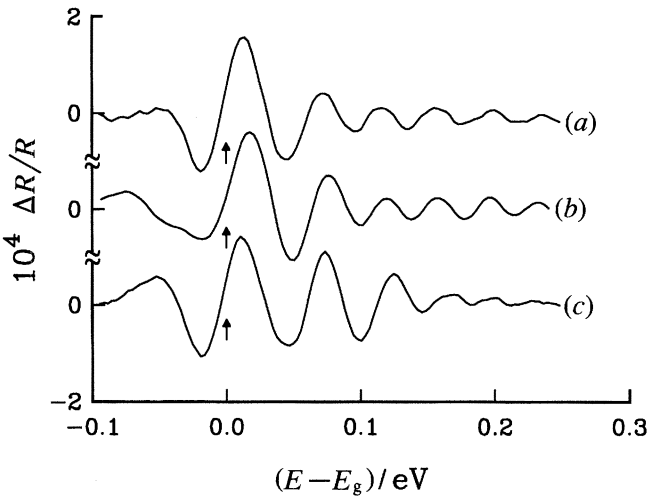

Figure 5. $In_{0.53}Ga_{0.47}As/InP$; photoreflectance 300 K: (*a*) sample A, $E_g = 0.759$ eV; (*b*) sample B, $E_g = 0.751$ eV; (*c*) sample C, $E_g = 0.727$ eV.

Table 1. *Barrier height or interface Fermi level* ($E_F - E_V$ eV)

material	I–V	PR	IP
metal–GaAs	0.6–0.8[b]	0.7[c]	—
As–GaAs[a]	0.7	0.7	—
GaAs:As	—	0.7	0.7
LT–GaAs	—	0.93–1.0	—
AlGaAs:As	—	—	0.93
GaInAs:As	—	0.49	—

[a] Rossi (1987); [b] Waldrop (1984); [c] Yin (1992).

(Glemboki & Shanabrook 1992). The obtained band gap energies are indicated by the arrows and also are listed. The FKO spectra were used to calculate either the surface Fermi levels for GaInAs or the bulk pinned values in GaInAs:As. After including the Debye length correction we find Fermi levels of $.0.49 \pm 0.03$ V, 0.47 ± 0.03 V and 0.53 ± 0.03 V above the valence band edge for samples A, B and C respectively.

It should be noted that if the GaInAs:As does not pin the Fermi level, then, due to the differences in undoped GaInAs thickness between samples A, B and C, the electric fields in samples A and B would have to have about one half the value of sample C in order for the Fermi levels at the surface to be the same for all three samples, which is clearly not the case. Thus it is seen that the Fermi level is pinned at nearly the same value for both GaInAs surfaces and GaInAs:As. It should also be noted that the surface Fermi level pinning value for GaInAs found in the present study is close to that observed in previous reports (Wieder 1981; Kajiyama *et al.* 1973).

The pinning value for GaInAs:As and the values measured for GaAs:As and LT–GaAs (Warren *et al.* 1992; Shen *et al.* 1992) along with the pinning values for GaAs:As and GaAlAs:As from the IP data of figure 4 are shown in table 1. Several points should be noted. First is both the qualitative and quantitative differences between LT–GaAs and GaAs:As. For GaAs:As Fermi level pinning occurs at 0.75 eV above the valence band edge irrespective of the doping type of doped layer I in the

samples. This means that As precipitates in GaAs:As can trap both electrons and holes at a single energy and, hence, acts like a normal metal–GaAs Schottky barrier. On the other hand LT–GaAs pins the Fermi level when the doped layer I is p-type but not when it is doped n-type (Warren *et al.* 1992; Shen *et al.* 1992). This shows that the pinning sites in LT–GaAs, i.e. either As anti-site defects or As interstitials, have donor character but not acceptor character. Thus the results of this experiment do not support the notion that anti-site defects are associated with Fermi level pinning at pinned metal–GaAs interfaces.

The second point is that pinning energies for GaAs:As and GaInAs:As are close to the values observed at pinned metal–GaAs and metal–GaInAs interfaces. This coupled with the IP results in table 1, provide consistent results over a wide range of materials and different characterization techniques which support the notion that As precipitates in GaAs, GaAlAs and GaInAs act as Schottky barriers whose barrier heights are well characterized by the Schottky model using the As work function and semiconductor electron affinities.

6. Summary

We have reviewed some recent progress made towards forming unpinned III–V compound semiconductor surfaces and interfaces. We have shown that dielectric–GaAs interfaces can be formed with greatly reduced interface state densities. We have also shown that metal–(100) GaAs interfaces can be formed with barrier heights which approach the Schottky limit. This is in contrast with previously observed pinned interfaces. Finally, we have shown that As precipitates in layers of GaAs, AlGaAs, and GaInAs form Schottky barriers and that the barrier heights closely match those observed at pinned metal interfaces for these materials. These results taken together demonstrate the usefulness of the EWF model in accounting for the electronic behaviour of III–V semiconductor surfaces and metal interfaces.

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