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Study of Interfacial Chemistry between Metals and Their Effect on Electronic Systems

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A number of results are summarized in this report. Many of these relate to the Advanced Unified Defect Model outlined in the previous semi-annual report. In this context, the modelling results help explain recent results on a model ohmic contact from Waldrop. This is important in that it appears that a new mechanism for ohmic contacts on GaAs is possible.

Another area of research is that of heterojunctions. In one set of experiments, new techniques involving polarization dependent SEXAFS (Surface Extended X-ray Absorption Fine Structure) measurements were developed and applied to determine the lattice constant of Si on GaAs perpendicular to the interface as a function of Si thickness. The results indicate dislocation formation at these 4% lattice mismatched heterojunctions at Si thicknesses less than previously predicted.

Our work on Si/GaAs has allowed us to critically examine the roles of materials perfection and measurements difficulty in determining offsets using PES. We find that differences in reported results are likely due to prior misinterpretation of experimental data rather than a variation of offset due to materials imperfection.

A new soft X-ray source allows us to use this tool with high surface sensitivity in PES. The effects of annealing of Ti/GaAs give important insights for this practically important system. Studies of As/GaAs gives more insight into the nature of Fermi level pinning on GaAs.

1. Modelling of metal/semiconductor interfaces

Modelling for the interfacial Fermi level based on the Defect model was developed. The basis of the model is the charge neutrality principle, where a sample in nominal electrical equilibrium with its environment has no net charge in the near-surface and surface region. On a surface which has a thin non-metallic overlayer, the charge in the depletion region and the charge in induced defect states is equal and opposite to maintain the charge neutrality. The calculation proceeds by adjusting the Fermi level until this condition obtains. This gives the quantitative prediction of the defect model for the interfacial Fermi level position as a function of coverage for thin semiconducting overlayers. If the overlayer is metallic, the charge which terminates any electric field at the surface of the metal is included also. With this addition, the modelling predicts the Fermi level pinning position as a function of coverage.

The charge neutrality model was evaluated with input parameters relevant to a study of heavily doped layers between the bulk GaAs and metal. This structure was proposed as a model ohmic contact by Waldrop et. al.[1]. When the Fermi level is near the conduction band minimum, the Schottky barrier height is low. The barrier is also narrow, facilitating tunnelling. Empirically, they find that the heavily doped overlayer can move the Fermi level to the conduction band minimum, even when a metal overlayer is added. This surprising result can be explained by applying the modelling developed here to their results. The results from adding a heavily doped semiconducting overlayer are shown in Fig. 1. The metal overlayer was added to the modelling also (not shown) and the Fermi level remains near the conduction band minimum. Thus we find that their results can be explained by the charge produced by the donors, and their results are consistent with the defect model.

The quantitative evaluation of the Defect model has also provided the explanation for experimental data from this research group regarding the Ge/InP interface. The charge from the heavily doped overlayer is included in the charge balance equation and the result is that for heavy enough n-type doping, the Fermi level can be pulled up to the conduction band minimum. This provides a physical explanation for the unusual band bending discovered for the Ge/InP interface which is grown at 20°C substrate temperature[1].

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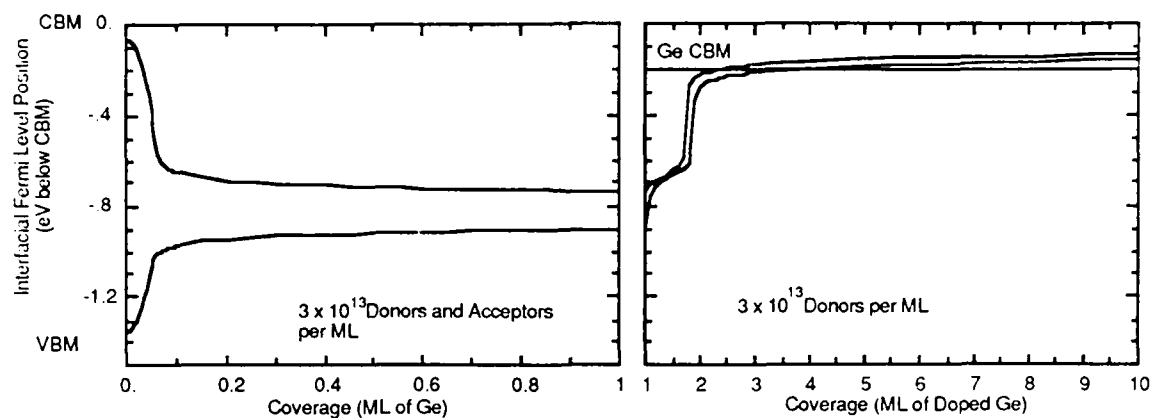


Figure 1

The interfacial Fermi level position as a function of overlayer coverage is shown above. Two curves are shown, the top one for the n-type substrates and the bottom one for p-type substrates. It is assumed that there are 3×10^{13} defect donors and acceptors formed per monolayer for the first monolayer. After that, no more defects are formed, but instead, doping donors are added at the same rate.

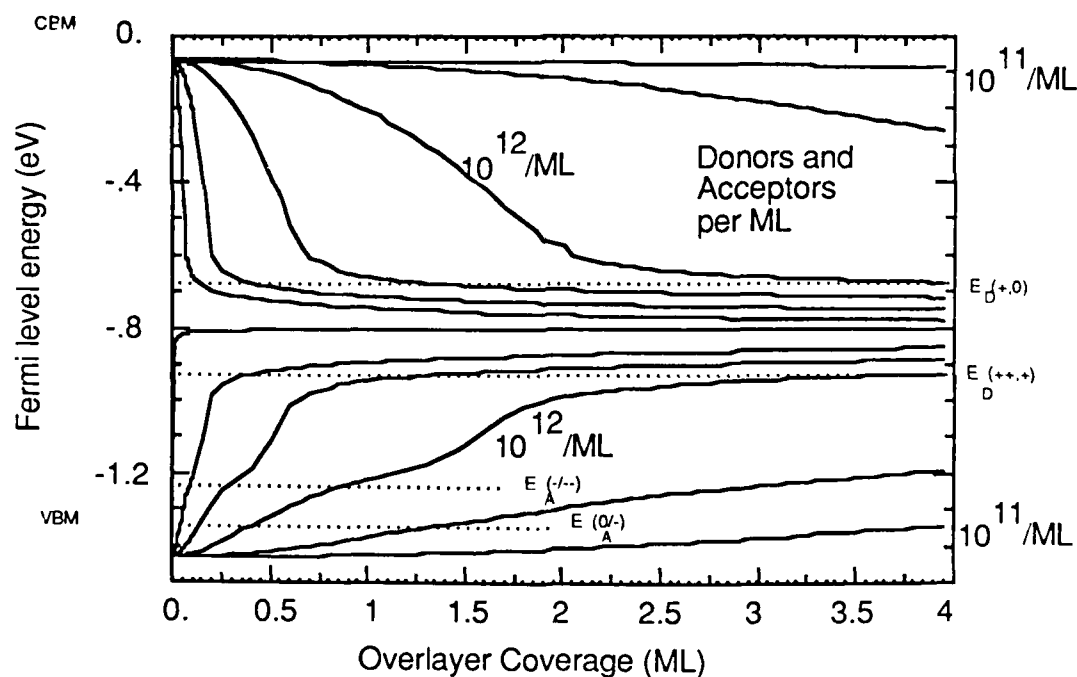


Figure 2

The interfacial Fermi level energy as a function of overlayer coverage for the donor and acceptor levels of the Advanced Unified Defect Model. The curves starting near the conduction band minimum at zero coverage are for n-type substrates; at the valence band maximum for p-type. Each of the curves represents a different assumption about how many defects are generated per monolayer of coverage.

The modelling was extended to provide quantitative predictions of the Fermi level behavior as a function of coverage for the Advanced Unified Defect model. This new model associates the defects which are responsible for the Fermi level pinning at the Schottky barrier with the EL2 level which has been studied for the bulk GaAs and is responsible for the semi-insulating GaAs. The model is described in detail in our previous reports. The results are shown in Fig. 2, and at least two conclusions can be drawn from this figure. One, in order to obtain pinning positions near the EL2 donor states, one needs about 50% more of these donors than the background acceptors. Secondly, the pinning positions will not be exactly on the EL2 levels, but will instead be near them, and the exact position depends on the density of the donor levels.

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2. Dislocation Formation in Large Lattice Mismatched Heterojunctions

During this period we studied the dislocation formation in the 4% lattice mismatched Si / GaAs (110) heterojunction. For a system with such a large mismatch, equilibrium energy minimization calculations by Van de Merwe predict the formation of dislocations starting at a 5 ML coverage with measurable residual strains persisting in the Si overlayer for coverages larger than 50 ML. We performed a polarization dependent SEXAFS, surface extended x-ray absorption fine structure, measurement of the anisotropic strain in thin Si overlayers grown on the GaAs (110) substrate. We found significant dislocation formation at a 4 ML coverage, below the predicted critical thickness of 5 ML. Furthermore the residual strain was no longer measurable in our system for coverages greater than 16 ML. Our results suggest more rapid dislocation formation than predicted by theory and greater difficulty in growing dislocation free strained layer structures and superlattices.

3. Photoemission Measurements of Valence Band Discontinuities: Effects of Non-idealities

We report an overview of our valence band discontinuity measurements and those by others on the Si / GaAs (110) heterojunction in an attempt to explain the wide scatter in the experimentally reported values. Such a critical review has recently become necessary since the progress in understanding heterojunction band line ups has increasingly become dependent upon the availability of accurate and reliable discontinuity measurements. The large scatter in experimentally determined discontinuities not only makes the evaluation of different theories difficult, but it raises the technologically important question as to the control we might have over this important electrical parameter.

We critically evaluate the possibility of variations in the valence band discontinuity for the Si / GaAs (110) heterojunction measured by photoemission under a wide range of growth conditions which affect the overlayer crystalline order, strain and chemical reactivity. We find no measurable differences in the band offset under any of the above growth conditions. Apparent variations are a result of non-idealities such as chemical shifts and defect states which invalidate the simple assumptions of the measurement technique and require more careful interpretation of the data. Such results emphasize that photoemission discontinuity measurements, like electrical or optical measurements, are model dependent and are subject to misinterpretation.

4. New Soft X-ray Source: Recent Applications

The new Zr anode soft x-ray source has added valuable new experimental capabilities to our laboratory. Not only have the large photoionization cross section and inherent surface sensitivity of the new source been useful in the band bending and chemical studies of overlayers on GaAs substrates, but the 151 eV x-ray energy enables us to monitor core levels normally masked by the large cross sections of other levels at deeper x-ray or softer ultraviolet photon energies. This capability is due to the large variation in the photon energy dependence of the cross section for different core and valence band levels. The custom fabricated 1500 Å graphite window has been shown to be important in both preventing the contamination of the sample and in permitting the transmission of an appreciable fraction of soft x-rays.

5. Studies of the Effects of Annealing Thin (0.3-3.3 ML) Ti Overlayers on GaAs(110)

Using soft x-ray (SXPS), x-ray (XPS) and ultraviolet (UPS) photoemission spectroscopies, we studied the chemical reactions and electronic properties of thin (.3-3.3 ML) Ti overlayers on GaAs(110) deposited at room temperature and then annealed to $\sim 400^\circ\text{C}$. Analysis of the substrate and overlayer core levels and the valence band shows a rapid change in the interfacial reaction products upon annealing. For these overlayer thicknesses, decomposition of the Ga 3d spectra into a substrate (Ga in GaAs) and reacted component shows that at room temperature, the major contribution is that due to elemental Ga, rather than the dilute Ti-Ga alloy observed for thicker coverages[1]. Upon annealing, the substrate component increases in intensity; the energy of the reacted Ga shifts to higher binding energy, suggesting either the formation of a Ga-rich Ti-Ga alloy or islanding of the Ga at the surface. The reacted As 3d components shift slightly from their room temperature positions to lower binding energy and stabilize at energies consistent with those reported previously for thicker coverages (6.7 ML) after annealing; curve fitting analysis suggests two Ti-As compounds. We also observe a slight increase in intensity of the reacted As near the surface. The valence band studies suggest a movement of Ti into the substrate, as there is a sharp decrease in the Ti 3d contribution near the valence band maximum (VBM). Electrical measurements on diodes prepared and measured in ultrahigh vacuum show an increase of 0.1 eV in the Schottky barrier height on n-GaAs when annealed to 330°C . The PES valence band studies also show this shift in Fermi level position. The relationship between the interfacial chemical reactions at elevated temperatures and the Schottky barrier height appears to be related to the changes in the concentration of As-related defects near the interface. In particular, for the advanced defect model[2], the increase in barrier height is associated with a decrease in excess As near the interface due to the reaction of As with Ti and liberation of Ga, and thus a decrease in As_{Ga} antisite double donors. Excess Ga could form Ga_{As} antisite compensating acceptors which would help in moving the Fermi level toward the VBM and thus increasing the barrier height on n-GaAs.

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6. Arsenic on GaAs: Fermi Level Pinning and Thermal Desorption Studies

It is becoming increasingly apparent that excess As is emerging as a key issue in understanding the surface and interfacial properties of GaAs. The "effective work function" model is based on excess As on the GaAs interfaces [1]. For the defect model, it has been suggested that the key defect is the As_{Ga} antisite and that the presence of excess As is necessary to explain a wide variety of interfacial phenomena [2,3]. Therefore, the growth of an arsenic overlayer on GaAs should help elucidate many of these points.

To perform the growth of an arsenic overlayer on GaAs, a sample preparation chamber, separate from the surface analysis chamber, was constructed. This is to prevent contamination of the surface analysis chamber with toxic arsenic. Also, the As over pressure required during the growth of an arsenic overlayer is quite high, so the use of the sample preparation chamber helps maintain a good vacuum in the surface analysis chamber. The sample preparation chamber and the surface analysis chamber are coupled together using a gate valve and a magnetically-driven sample transfer mechanism.

We grew arsenic overlayers on freshly-cleaved, clean GaAs surface at room temperature. The coverage of As on the GaAs surface appears to reach saturation at about 1ML of As. This is also the coverage at which the GaAs surface fermi level is pinned. The pinning positions are 0.5 eV above VBM (valence band maximum) for both n- and p-type GaAs. Upon annealing at 500°C (below 580°C, there is no significant evaporation of Ga or As from GaAs [4]), the deposited As overlayer is desorbed from the surface and the surface fermi level moves back almost to the bulk position. (0.2 eV below CBM [conduction band minimum] for n-GaAs and 0.1 eV above VBM for p-GaAs. CBM and VBM are the bulk fermi level positions.) These results are in agreement with the "effective work function" model. The defect model predicts in general two different pinning positions for metals on n-type GaAs (0.75 eV above VBM) and p-type GaAs (0.5 eV above VBM). However, arsenic has a relatively high electronegativity value, so the As overlayer may take electrons from the singly ionized donor state (0.75 eV above VBM), keeping the As_{Ga} antisite in the doubly ionized donor state (0.5 eV above VBM). Thus, both n-type and p-type GaAs pin at 0.5 eV above VBM, which is similar to the situation for Cu, Pd, Pt, Au with electronegativities (1.9, 2.2, 2.2, 2.4) close to that of As (2.0).

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Semi-annual Financial Report

1 April 1987 to 30 September 1987

N00014-83-K-0073

I.	Amount currently provided for in contract period	\$1,090,000
II.	Expenditures and commitments to 30 September 1987	
	A. Expenditures	1,146,327
	B. Commitments	35,154
III.	Estimated funds required to complete Year 2	<91,481>
IV.	Estimated date of completion of Year 2	30 September 1987