Measurement of Deep Levels at InGaAs(P)/InP Heterojunctions (unclassified)

We have studied the properties of semiconductor heterojunctions using several novel analytical and experimental techniques. A new, and highly accurate means for measuring the properties of heterojunctions has been demonstrated, where the measurements of the band offset energies can be made even in the presence of high densities of interface charge. The techniques developed have been applied to study both InGaAs/InP as well as HgCdTe/CdTe heterojunctions, affording the most accurate measurements obtained to date for the band offset energies of these materials systems. These measurements were made possible via the use of novel test structures consisting of organic-on-inorganic semiconductor contact barrier diodes. Furthermore, we have grown InGaAs/InP heterojunctions with the lowest defect densities yet reported, and obtained the surprising result that the defect charge density is independent of the degree of lattice mismatch. We observe that the defect density is strongly related to the purity of the source metals used in the semiconductor growth. Finally, we have employed our low defect density heterojunctions...
19. continued...
in novel, high sensitivity heterojunction bipolar phototransistors.
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Measurement of Deep Levels at InGaAs(P)/InP Heterojunctions

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I. Introduction
In this report, we discuss the principle achievements of a three year program whose purpose was to investigate the sources of deep levels universally observed at InGaAs(P)/InP heterojunctions. Due to the utility of these heterojunctions for long wavelength optical communications systems, it is extremely important that we understand fully those properties of the materials which influence optoelectronic device operation. Indeed, the quality of the heterojunction plays a major role in device characteristics, and hence our interest in this subject. To study the heterojunctions, several unique tools were conceived in our laboratory. These tools involved the use of organic-on-inorganic (OI) semiconductor contacts, and have broad applicability to other materials systems, such as HgCdTe/CdTe, which was also explored in this research.

Details of some of the technical aspects of this program have appeared in four full technical journal articles (Appendix 1), a fifth paper which is currently
under review at Applied Physics Letters (Appendix 2), and one paper still in preparation to be submitted to the Journal of Applied Physics. Additionally, we have given two oral presentations (one at the First International Conference on InP and Related Compounds, and one at SPIE), and one patent application which is presently under review by the U.S. Patent Office.

Practical aspects of this work are also now being employed by at least two companies (Epitaxx, Inc. and Santa Barbara Focalplane) to assist in product commercialization. A third company (Santa Barbara Research Center) has taken sufficient interest in our results such that they are co-authors of the patent application. We note that this program has been critical to understanding and improving III-V semiconductor materials for use in optoelectronic circuits.

The major accomplishments of this three year program are highlighted below:

1) A theory for the measurement of heterojunction offsets in the presence of interface defects was developed for the first time. This theory is a significant extension of the method of Kroemer [1,2] for measuring band offset energies via C-V methods. In fact, the simple application of our theory to measurement provides for the ability to separate out the effects of interface defects from the actual offset energy. To our knowledge, this is the most accurate method available for measuring heterojunction band offset energies, surpassing other "conventional" techniques such as multiple quantum well luminescence and absorption, XPS, and current transport methods. It is simple to apply, and is relatively free of the need to employ numerous parameters of which the investigator has only a vague knowledge.

2) The validity of the theory was tested experimentally on both VPE and LPE grown InGaAs/InP heterojunctions. The VPE samples were obtained in a collaborative effort with Epitaxx, Inc., whereas we grew the LPE samples in our laboratory. During the course of this experimental work, we demonstrated the first InGaAs/InP heterojunctions which do not show evidence for a high defect density at the heterointerface. Indeed, using ultra high purity In source metals, we have achieved the lowest interface defect densities (by one order of
magnitude, or more) ever reported for InGaAs/InP heterojunctions. Furthermore, we have found that the defect density is unrelated to lattice mismatch, suggesting the source of defects is due to impurities in the source metals and gases used during growth.

3) The methods of using organic contacts in conjunction with our energy offset theory was applied to make the first measurements of HgCdTe/CdTe valence band offsets using C-V techniques. We obtained the surprising result that the HJ offset is of the Type II (rather than Type I) variety, contradicting conventional wisdom. Although there is some previous, weak data from other groups which infer a Type I junction, we are aware of at least one very recent report confirming the Type II geometry. Clearly more work needs to be done here to totally eliminate sample and growth-induced peculiarities. However, the organic method of C-V analysis on narrow band-gap materials is an important step in expanding our knowledge of these useful semiconductors. Furthermore, our results suggest many room temperature device possibilities for IR detectors using the organic/inorganic semiconductor approach.

4) Work on localized defects at heterojunctions was extended to the understanding of InGaAs/InP bipolar phototransistors (HPTs). Our modelling indicates that placement of low-doped layers within the base or emitter regions can result in a significant increase in the photocurrent gain at low input power intensities. This finding has already resulted in a marked improvement in HPT sensitivity at low input optical powers, thereby making these devices excellent candidates for integration in bipolar optical receivers (an approach which has generally been ignored due to the low sensitivity of HPTs at low input optical powers).

We now discuss in greater detail the specifics of these results.

2. Summary

1) Heterojunction offset theory

There have been long-standing controversies of the role that defects play in both heterojunction measurement and performance. Figure 1 shows a calculation of the apparent free carrier concentration profile in the presence of
various amounts of interfacial charge, $\sigma_i$. The effect of charge on the profile is readily apparent. We note that this variation in the profile has importance since it indicates a variation of the diffusion potential with $\sigma_i$, which is responsible for controlling charge transport in heterojunction devices. In Fig. 2 we show that the measured value of the offset energy, $\Delta E_c$, depends strongly on the interface defect density. It would seem from this that extracting the "true" value of $\Delta E_c$ from C-V data (or any data) would be extremely difficult. However, in this ARO-sponsored program, we developed a very simple technique for determining $\Delta E_c$ even when charge exists at the heterojunction. Note that this technique is only valid if the charge is monopolar in nature -- dipolar defects would be indistinguishable from the intrinsic dipoles which form the heterojunction offset due to their spatially averaged charge neutrality. For this measurement technique, we generated a series of "universal" curves (Appendix 1) which are useful for obtaining an accurate determination of $\Delta E_c$ from the $n(x)$ profiles such as those shown in Fig. 1. The heterojunction diffusion potential for a defect-free heterojunction ($V_D(0)$) from which $\Delta E_c$ is directly related, is determined using the measured potential, $V_{DK}$, along with:

$$V_D(0) = V_{DK} + \frac{q}{\kappa}[\sigma_i(\Delta x_j - d/2) - (N_{D2} - N_{D1})\Delta x_j^2/2]$$

To obtain $V_D(0)$, therefore, all we need to do is measure $V_{DK}$ and $\sigma_i$ using a standard technique such as Kroemer's method, determine the interface width, $d$, using SIMS, for example, and plug the values into the above equation.

This procedure has been used on samples grown by hydride vapor phase epitaxy (VPE) and by liquid phase epitaxy (LPE). In Fig. 3, we show a typical measurement made on a VPE InGaAs/InP heterojunction, giving the most accurate value for such heterojunctions measured to date by C-V or other methods.

ii) InGaAs/InP heterojunctions with very low interface state densities

During the course of our investigations of heterojunctions, we grew many InGaAs/InP samples with remarkably low interface state densities. These samples were grown in our high uniformity LPE system, using ultra-high purity indium for the melt sources. In all previous work done both in our lab as well as
in other labs around the world [3,4,5], it has been found that InGaAs/InP heterojunctions have a high defect density (with $\sigma_i > 10^{11}$ cm$^{-2}$) such that the apparent $\Delta E_c$ is observed to vanish as $T \to 0$. For our samples, it was found that this effect was either greatly reduced, or even eliminated due to a significant decrease in the interface state densities obtained by our growth techniques.

A sample which demonstrates a small decrease in the measured $\Delta E_c$ is shown in Fig. 4. Here, it is observed that there is no significant decrease in $\Delta E_c$ of approximately 70 meV at 150K -- already a significant improvement in the typically observed decrease of 200 meV reported by others. As proof that this decrease is in fact due to interface states filling at low temperature (a point which in itself has generated considerable controversy), we have used the simple theory and equation given above to "correct" the measured values of $\Delta E_c$ by subtracting the effects due to traps. Note that the traps were observed independently using DLTS. The corrected temperature dependence of $\Delta E_c$ is shown in Fig. 5. From these data we obtain the expected result -- i.e. the intrinsic value of $\Delta E_c$ is independent of temperature since it can only be a function of the dipolar character of the interfacial atoms at the heterojunction.

In addition to growing samples with low $\sigma_i$, we have also grown material which is evidently free of any significant defect density. This is confirmed by the plot in Fig. 6 which indicates no variation of the measured $\Delta E_c$ versus temperature or frequency. To our knowledge, this is the only demonstration of an InGaAs/InP heterojunction which has no significant defect density. Furthermore, we observe that there is no dependence of the offset energy on lattice mismatch, even though the mismatch was varied from sample-to-sample over the extremely large range of $\pm 0.25\%$. Indeed, the defect densities measured for these samples are the lowest ever reported (with $\sigma_i < 7 \times 10^9$ cm$^{-2}$), again independent of lattice mismatch. We attribute this high quality interface to extremely good control of temperature during growth, and the elimination of defects due to the melt-back process. However, the main source of these high quality interfaces is probably a result of the use of very high purity In melts (with 7 9's+ purity). This may be an indication that LPE is still the growth technology capable of giving the lowest defect density growth attainable. One further interesting outcome of this work is the observation that defects resulting from misfit dislocations are not always electrically active at the heterojunction. We conclude that the energies of such defects might be "pulled" into the conduction or valence bands at the heterointerface, and hence they
remain permanently thermalized. This conclusion appears consistent with the observation in previous work that heterojunction defects are shallow [3].

iii) HgCdTe/CdTe heterojunctions

We also investigated IR materials after we discovered that certain organic compounds make good rectifying contact to the narrow band gap (0.24 eV) Hg$_{0.7}$Cd$_{0.3}$Te. The "traditional" compounds used in organic contacts, such as 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA), do not form rectifying contacts on these semiconductors, possibly due to the oxygen in the organic molecule reacting with the Hg. Thus, we chose a class of crystalline organic materials which did not contain oxygen -- i.e. the phthalocyanines (Pc's) -- and found that indeed, good rectifying organic-on-inorganic (OI) semiconductor devices were obtained. The room temperature, bipolar I-V characteristics of such devices are shown in Fig. 7. Note that reverse-biased breakdown voltages as high as 8V were observed at room temperature. This is to be compared with < 0.5V observed for metal/HgCdTe junctions. Due to this observation, the prospects for room temperature IR device operation are quite promising.

The OI device is fabricated by first depositing, in vacuum, approximately 1000 Å of the pre-purified organic material onto the wafer surface following procedures described in detail elsewhere [6,7]. Next, ohmic contact is made to the substrate by depositing a suitable metal across the wafer surface. This is followed by depositing ohmic contact dots onto the organic material surface. The OI diode area is defined by the diameter of the contact dot due to the anisotropy in the organic film conductivity which confines current to flow only beneath the dot. We note that for semi-insulating substrates, the "back contact" can be deposited directly onto the wafer surface near to the contact dot. Alternatively, this back contact can also be deposited onto the organic film surface. As long as this back contact is larger than the dot contact, little or no error is incurred in data obtained using this structure.

Capacitance-voltage analysis is carried out using the OI structure along with analysis techniques which are applied to the study of Schottky barrier or p-n junction diodes. The OI diode provides the advantage of being easy to apply and non-destructively remove from the wafer surface (using positive photoresist
developer), and large reverse voltages can also be applied to allow for deep depletion into the wafer bulk.

We have used the OI diode to obtain information regarding doping and heterojunction offsets which have heretofore been inaccessible to C-V analysis. Figure 8 shows a composite free carrier concentration profile obtained on a taper-etched, n-HgCdTe/p-HgCdTe/P-CdTe sample. To obtain such a deep depletion profile (extending 10 μm below the surface) through both p and n-type materials, it was necessary to taper-etch the epitaxial layers in this sample prior to deposition of the H₂Pc organic thin film. These data indicate that the OI device is useful in probing both n and p-type material, and can also be used on narrow bandgap as well as wide gap semiconductors. A detailed view of the carrier concentration at the p-P heterojunction is shown in Fig. 9. Here, the results are truly surprising. It is apparent that hole depletion occurs on the HgCdTe side, whereas accumulation occurs on the CdTe side of the heterointerface, suggesting the band diagram shown in the inset of the figure. While the offset direction is opposite to that understood to be the case by conventional wisdom, the unique aspect of C-V analysis is that the band structure does not have to be guessed at a priori (as in the case of optical measurements, for example). Rather, the band structure and the dipole direction is directly inferred from the relative positions of the spike and notch in the free carrier concentration profile.

Once again, ΔE_c was measured from these data using our theory developed earlier. We obtained ΔE_c = 110 ± 20 meV and σ_i = -6 x 10¹⁰ cm⁻². These values were checked by a full solution to Poisson's Equation, shown by the dashed line fit in the figure.

iv) High sensitivity heterojunction bipolar phototransistors

We have also investigated the effects of interface charge on the operation of heterojunction phototransistors (HPTs). Here, we fabricated standard HPTs using an n-InP emitter/p-InGaAs base/n-InGaAs collector grown by LPE. Due to the high quality heterointerfaces, we fabricated transistors with very low output conductances, as shown in Fig. 10. Here, P_in is the input optical power. These transistors showed the common problem of decreased gain at low input power levels (Fig. 11). This is due to a combination of effects, most notable among which are bulk and surface recombination in the base-emitter...
region. To make a transistor useful at very low input optical powers which are needed for detection in most photonic transmission systems, however, this effect at low $P_{in}$ must be greatly reduced, or even eliminated.

The recombination current is exacerbated by the presence of the dip in the conduction band at the E-B junction. This provides a recombination site for electrons injected into the base region, thus decreasing the gain, especially at low injection levels. To eliminate this problem, we investigated the device shown in Fig. 12. This is only a minor modification of the standard HPT in that a very thin (100 - 500 Å) n-layer is inserted at the emitter side of the E-B junction. This results in a flattening out of the conduction band at the heterointerface eliminating the electron trap to a considerable degree. Also, it provides a higher "ramp" over which the electrons are injected at the E-B junction, thus allowing them to avoid trapping in the remaining dip. Finally, it also reduces E-B capacitance, thus improving high bandwidth response.

The effect on gain for this "novel" device is shown in Fig. 11. It is clearly apparent that the doping dip enhances the gain at low input power levels (corresponding to low collector currents). The ideality factor of these gain curves, which is related to the slope of the curves, is found to be equal to 1.2 at low current levels corresponding to the best values obtained to date for LPE heterojunction phototransistors. More important is the fact that the novel structure has a significantly lower ideality factor than the conventional structure (with a value of 1.7).

3. Conclusions

In conclusion, we have studied the properties of semiconductor heterojunctions using several novel analytical and experimental techniques. A new, and highly accurate means for measuring the properties of heterojunctions has been demonstrated, where the measurements of the band offset energies can be made even in the presence of high densities of interface charge. The techniques developed have been applied to study both InGaAs/InP as well as HgCdTe/CdTe heterojunctions, affording the most accurate measurements obtained to date for the band offset energies of these materials systems. These measurements were made possible via the use of novel test structures consisting of organic-on-inorganic semiconductor contact barrier diodes. Furthermore, we have grown InGaAs/InP heterojunctions with the lowest defect densities yet reported, and obtained the surprising result that the defect charge
density is independent of the degree of lattice mismatch. We observe that the
defect density is strongly related to the purity of the source metals used in the
semiconductor growth. Finally, we have employed our low defect density
heterojunctions in novel, high sensitivity heterojunction bipolar phototransistors.

4. Acknowledgements

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the theory, concepts and data used in this work. Also, I would like to thank Dr.
Michael Stroscio for his steadfast support of this program.

5. References

   295 (1980).


FIGURE CAPTIONS

Fig. 1: Calculated free carrier concentration as a function of position for several values of fixed interface charge density. The heterojunction studied is shown in the inset.

Fig. 2: Dependence of the measured conduction band offset energy as a function of fixed interface charge density. Here, $\Delta E_{ck}$ is the measured value, $\Delta E_{c1}$ is due to the contribution from fixed charge only, and $\Delta E_{c}$ is the actual value.

Fig. 3: Calculated (dashed line) and measured (solid line) apparent free carrier concentration profiles for a VPE-grown InGaAs/InP heterojunction. SIMS profile of the heterojunction is shown in the inset.

Fig. 4: Dependence of the measured conduction band offset energy as a function of temperature for various measurement frequencies. Sample is a InGaAs/InP heterojunction grown by LPE.

Fig. 5: Data of Fig. 4 after correction using Eq. (1) in text.

Fig. 6: Dependence of the measured conduction band offset energy as a function of temperature for various lattice mismatches. Samples are InGaAs/InP heterojunctions grown by LPE using ultra-high purity indium.

Fig. 7: Bipolar current voltage characteristics of an H$_2$Pc/p-HgCdTe heterojunction measured at room and low temperatures.

Fig. 8: Composite free carrier concentration profile of a taper-etched n/p-HgCdTe/CdTe sample.

Fig. 9: Detail of the profile shown in Fig. 8 in the region of the HgCdTe/CdTe heterojunction. Inset is the inferred band diagram for this sample.
Fig. 10: Heterojunction bipolar phototransistor characteristics obtained using LPE growth.

Fig. 11: Photocurrent and dark current gains of novel (Fig. 12) and conventional InGaAs/InP HPTs as a function of collector current.

Fig. 12: Novel InGaAs/InP heterojunction bipolar phototransistor structure with low base recombination current.
Fig. 1

Graph showing the relationship between \( n^* (x^*) \times 10^{15} \text{cm}^{-3} \) and \( x \text{(Å)} \).

- \( \sigma_i = 1 \times 10^{11} \text{}/\text{cm}^2 \)
- \( 5 \times 10^{10} \text{}/\text{cm}^2 \)
- \( -2 \times 10^{11} \text{}/\text{cm}^2 \)
- \( -5 \times 10^{10} \text{}/\text{cm}^2 \)
- \( -1 \times 10^{11} \text{}/\text{cm}^2 \)

Inset: Schematic of the trap region with \( d = 100 \text{ Å} \).
Fig. 2
Fig. 3

\[ \Delta E_c = -0.24 \text{ eV} \]
\[ \sigma_i = 2.7 \times 10^{10} \text{ cm}^{-2} \]
\[ d = 350 \text{ Å} \]
Fig. 4

Apparent Conduction Band Offset (eV)

Temperature (K)

Sample #1

* 1 MHz
□ 400 KHz
△ 200 KHz

0.25 0.20 0.15 0.10
Sample #1

Apparent Conduction Band Offset (eV)

Temperature (K)

* 1 MHz
□ 400 KHz
△ 200 KHz
Fig. 6

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<tr>
<td>○</td>
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<tr>
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<tr>
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Measured Conduction Band Offset (eV)

Temperature (K)
Fig. 7

$H_2Pc/p-Hg_{0.7}Cd_{0.3}Te$
Fig. 8
Fig. 9
Fig. 10
Fig. 11

Photocurrent Gain (M)

Collector Current (µA)

Current Gain (β)

n = 1.75

n ≈ 1

n = 1.25

#1

#2

Photocurrent gain

Current gain
STRUCTURE OF HETEROJUNCTION PHOTOTRANSISTOR

Au-Sn CONTACT

n: InGaAs COLLECTOR

p: InGaAs BASE

Au-Sn CONTACT

N⁻ InP EMITTER

N: InP EMITTER

SI InP SUBSTRATE

Fig. 12
The determination of heterojunction energy band discontinuities in the presence of interface states using capacitance-voltage techniques

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Effects of trapped interface charge on the determination of heterojunction energy band discontinuity energies using capacitance-voltage (C-V) techniques are analyzed both theoretically and experimentally. We show that for shallow traps, whose charge occupancy is unchanged by variations in the applied voltage, the measured conduction band discontinuity energy ($\Delta E_c$) as determined by the depletion technique [Kroemer, Chien, Harris, and Edwall, Appl. Phys. Lett. 36, 295 (1980)] is a function of trap density ($\sigma_1$). This error source in determining $\Delta E_c$ is large for small values of $\Delta E_c$ due to distortions of the conduction band induced by the trapped interface charge. In addition, the analysis used for determining $\sigma_1$ and $\Delta E_c$ via the depletion technique has been generalized to correct for the effects of both deep and shallow traps. We show that at low measurement frequency, the measured value of $\Delta E_c$ is nearly independent of $\sigma_1$ and this value is near to the exact value of $\Delta E_c$ measured in the absence of interface traps (i.e., for $\sigma_1 = 0$). However, at high measurement frequency (or low temperature), the measured $\Delta E_c$ decreases with increasing $\sigma_1$ or increasing trap energy depth from the conduction band minimum. These deviations from the actual value can be corrected by using the equations developed in this article. We apply these results to the understanding of In$_{0.53}$Ga$_{0.47}$As/InP heterojunctions. The computer-simulated apparent free carrier concentration profiles are used to fit experimental data at several temperatures. The best fit value of $\Delta E_c$ ($= 0.22$ eV) is in agreement with the value obtained via the emended equations. We explain the complex temperature dependence of these experimental profiles as due to donor traps near the heterojunction.

I. INTRODUCTION

The band discontinuity energy is one of the most important parameters needed to determine heterojunction (HJ) characteristics. Among the various measurement techniques available, capacitance-voltage (C-V) analysis is among the most powerful. In particular, using the C-V method first proposed by Kroemer et al. and modified by Leu et al. information regarding the HJ position ($x_j$), the fixed charge density ($\sigma_1$), and conduction band discontinuity energy ($\Delta E_c$), can all be easily determined.

However, there are several phenomena which lead to inaccuracies in determining $\Delta E_c$ and related parameters by C-V methods. Among these are: compositional gradients between the contacting semiconductors; doping nonuniformities due to interdiffusion near the HJ; and the inherent difference between the actual $x_j$, and the apparent heterojunction depth ($x_j^*$) (as determined from the peak position of the apparent carrier concentration profile). As a result, the magnitude of the errors due to these factors needs to be studied in detail.

In particular, it has been observed that both $\sigma_1$ and $\Delta E_c$ obtained for In$_{0.53}$Ga$_{0.47}$As/InP heterojunctions measured by C-V techniques apparently depend strongly on both measurement and modulation frequency, contradicting the fact that $\Delta E_c$ is an inherent property of the HJ, and therefore should be independent of these "environmental" parameters. Recently, Kazmierski et al. pointed out that the dependence of $\Delta E_c$ on both temperature and frequency may arise from the dynamic behavior of interface traps. They suggest that the apparent carrier concentration profile, $n^*(x^*)$, with its characteristic peak and valley usually associated with the presence of the HJ dipole, can be generated entirely by deep donor traps, rather than due to a nonzero value of $\Delta E_c$. However, Kazmierski assumes that the donor traps are partially filled at low temperature, and completely filled at equilibrium at high temperature, which is opposite to what is expected for such traps. The dramatic shift of apparent ($x_j^*$) from the actual HJ position ($x_j$) used in their simulation was obtained by setting $\Delta E_c = 0$. This shift introduces large calculational errors, and thus the conclusion that $\Delta E_c = 0$ does not appear to be correct.

Lang et al. measured the conduction band discontinuity of the same HJ system by admittance spectroscopy of quantum well structures. In that work, a value of $\Delta E_c = 250 \pm 10$ meV was obtained which agrees well with the C-V data reported by others. On the other hand, Lang claims that C-V measurement yields a vanishing HJ diffusion potential at low temperature simply due to the presence of a parasitic temperature-dependent series resistance of the undepleted HJ region. This, however, contradicts data presented elsewhere.

In order to study the error sources inherent in C-V measurements of HJ properties, and to understand the apparent paradoxes mentioned above, the effects of shallow, as well as deep traps are considered by analytical as well as numerical simulation methods. The original equations of Kroemer et al. for the determination of the trap density ($\sigma_1$) and HJ diffusion potential ($\phi_D$) appear to be valid only for HJs with...
with a low density of shallow interface traps. It will be shown that \( \Delta E_c (\sigma) \)—i.e., the conduction band discontinuity energy measured for a HJ with a shallow interface charge density of \( \sigma \)—differs more from the actual value \( \Delta E_c (0) \) as \( \sigma \) increases, independent of the polarity of \( \sigma \). In addition, the deviation of \( \Delta E_c (\sigma) \) from the value calculated using the original equations suggested by Kroemer (called \( \Delta E_{cK} \) in this article) becomes nearly constant at high temperatures and low measurement frequencies. Modified equations are derived which can be used to correct for errors in \( \Delta E_c (0) \) induced by the presence of charge at the heterojunction. Also, the measured trap density obtained from the original equations (called \( \sigma_{K} \)) is found to deviate from the exact value of \( \sigma \), depending on whether the traps are donor- or acceptorlike.

Two In\(_{0.53}\)Ga\(_{0.47}\)As/InP heterostructure samples are studied by C-V techniques. For sample No. 1, we compare the experimental and theoretical C-V data measured at \( T = 201 \) and 102 K. The equations derived for determining the conduction band discontinuity were used to correct the measured value, \( \Delta E_{cK} \). After correction, the value of \( \Delta E_c (0) \) is found to equal 0.22 eV, which is consistent with the consensus of values of \( \Delta E_c \) for this HJ system reported in the literature. In a second sample, the apparent free carrier concentration profile shows a double-peak feature at room temperature on determining the consensus of values of \( \Delta E_c \) and the presence of charge at the heterojunction. Furthermore, carrier concentration profiles as obtained from C-V data are numerically simulated for the case of both deep and shallow levels, and the effects of measurement frequency and temperature on determining \( V_{DK} \) in the presence of deep traps are considered. In Sec. III, methods for obtaining \( \Delta E_c \), by use of the emended equations is presented. In Sec. IV, experimental data for In\(_{0.53}\)Ga\(_{0.47}\)As/InP HJs are analyzed and in Sec. V, we present conclusions.

II. THEORY

Figure 1 shows the apparent \([n^*(x*)]\) and actual free carrier concentration \([n(x)]\) profiles calculated for a Schottky barrier-on-heterojunction (SB/In\(_{0.53}\)Ga\(_{0.47}\)As/InP) structure. In this heterojunction system, In\(_{0.53}\)Ga\(_{0.47}\)As and InP have band-gap energies of 0.75 and 1.35 eV, respectively. The apparent (or measured) free carrier concentration \([n^*(x*)]\) is determined from C-V data obtained by depleting the HJ by applying reverse voltage to the adjacent rectifying SB contact. Hence, \( \Delta E_{cK} = \frac{-\int [N_D (x^*) - n^*(x^*)] dx^*}{q/\kappa} \),

with

\[ x^* = \frac{\kappa}{C}, \]

where \( x^* \) is the apparent distance from the SB contact, \( q \) is the electronic charge, and \( \kappa \) is the semiconductor permittivity.

The actual free carrier concentration profile \( n(x) \) is obtained by solving Poisson's equation. Due to the existence of a conduction band discontinuity \( (\Delta E_c) \), the free carriers are accumulated at the In\(_{0.53}\)Ga\(_{0.47}\)As side of the HJ. The difference between \( n^*(x^*) \) and \( n(x) \) in the HJ region (Fig. 1) arises from the limited spatial resolution inherent in the C-V data.\(^{23}\) Kroemer, and co-workers have shown\(^{10,11}\) that the total number of free carriers, as well as the first moment of the charge distribution should be identical for both the measured and actual carrier concentration profiles when integrated across the entire HJ region. Based on these assumptions, the density of fixed interface charge, \( \sigma_{K} \), and the diffusion potential \( V_{DK} \), of an isotype HJ can be expressed by

\[
\sigma_{K} = -\int_{x_0}^{x_1} [N_D (x^*) - n^*(x^*)] dx^*,
\]

\[
V_{DK} = q/\kappa \int_{x_0}^{x_1} [N_D (x^*) - n^*(x^*)] (x^* - x_j) dx^*,
\]

where \( N_D (x^*) \) is the background doping concentration at apparent position \( x^* \), and \( x_j \) is the actual position of the HJ as measured from the surface of the sample.

Now, the conduction band discontinuity \( (\Delta E_{cK}) \) is obtained from the diffusion potential via:

\[
\Delta E_{cK} = qV_{DK} + \delta_1 - \delta_2,
\]

where \( \delta_1 \) and \( \delta_2 \) are the depths of the Fermi levels as measured from the conduction band minima for the two contacting materials.

Note that only shallow interface charge traps are considered.
sidered in the above analysis. For deeper traps, whose occup-
cancies are a function of applied voltage, the density of ion-
ized traps \(\sigma_r\) changes with bias according to Fermi-Dirac
statistics. Hence, Eqs. (2) and (3) must be modified to ac-
count for variations in trap occupancy as the Fermi energy is
swep through the band gap in the HJ region.

To explore the effects that deep levels have on measure-
ments of \(\Delta E_r\), we assume that acceptor traps are nega-
tively charged when occupied by electrons, becoming neutral alter
the electrons are excited into the conduction band. On the
other hand, donor traps are positively charged when the
electrons are excited to the conduction band, and are neutral
when occupied. The density of ionized traps \(\sigma_r\) at each
voltage can be expressed by an integral over the ionized trap
concentration \(N_i(x)\) (+ for donor and − for acceptor traps). Hence, \(\sigma_r\) is given by

\[
\sigma_r = \pm \int N_i(x)dx
\]

and the diffusion potential obtained for a HJ with traps is
given by

\[
V_D(\sigma_r) = q/\kappa \int \left[ N_D(x) - n(x) \right] (x - x_j) dx.
\]

Both Eqs. (6) and (7) differ from Eqs. (2) and (3) in that the
actual \(n(x)\) rather than apparent \([n^*(x^*)]\) free car-
rier concentration profiles and positions are used. Fur-
thermore, note that Eqs. (6) and (7) may have an implicit vol-
tage dependence in the presence of deep traps. This
dependence arises via the means for determining \(n(x)\) using
\(C-V\) data. As voltage is increased, \(E_r(x)\) changes, which
will, in turn, contribute to \(n(x)\) via the emission of trapped
charge when \(E_r > E_f\). Defining

\[
n'(x) = n(x) \pm N_i(x)
\]

as the total free carrier concentration due to shallow plus
ionized deep donors (−) or acceptors (+), and substi-
tuting this along with Eq. (5) into Eq. (6) gives

\[
\int \left[ N_D(x) - n'(x) \right] dx = 0.
\]

Replacing \(n(x)\) with \(n'(x)\) is equivalent to setting \(\sigma_r = 0\).
Making the transformation of \(n(x) - n'(x)\) therefore should
allow for the determination of the "intrinsic" HJ diffusion
potential \(V_D\) from the potential measured in the presence of
defects. We will show that this can be accomplished without
the detailed knowledge of \(N_i(x)\) which, in fact, cannot be
exactly obtained using \(C-V\) data due to their limited resolu-
tion.

The diffusion potential in the absence of traps near the HJ \(V_D(0)\), is found by invoking the conservation of total
first moment of charge. Hence:

\[
V_D(0) = \frac{q}{\kappa} \int \left[ N_D(x) - n(x) \right] (x - x_j) dx,
\]

which leads to

\[
V_D(0) = V_{DK} \pm \frac{q}{\kappa} \int \left[ N_i^*(x^*) (x^* - x_j) dx^* \right].
\]

As will be shown below, the interface position apparently
"shifts" to \(x^*\) from its actual position \(x_i\), depending on the
interface state density \(\sigma_i\). Defining \(\Delta x = x_i - x^*\), we can
write Eq. (10) to obtain (for shallow or deep donor traps):

\[
V_D(0) = V_{DK} + \frac{q}{\kappa} \int \left[ N_i^*(x^*) (x^* - x_j) dx^* - q \Delta x / \kappa \right],
\]

where the upper sign refers to donors, and the lower to ac-
ceptors. Equations (11) and (12) are emended forms of Eqs.
(2) and (3). They can be used to determine the "intrinsic"
HJ diffusion potential \(V_D(0)\) using \(C-V\) data obtained for
HJs with a high density of trapped charge. We show below
that the original analysis\textsuperscript{10} is a special case of these
equations.

A. Shallow interface traps

If the acceptor energy level is well below the Fermi level
even at maximum applied voltage, or if the donor energy
level is well above the Fermi level even at \(V = 0\), all the traps
are ionized. In this case, the total density of ionized traps
\(N_i^*(x)\) is bias independent, and these shallow traps are
terred as "fixed charge traps." If we define the measured
total trap concentration \(N_i^*(x^*)\) in a manner analogous to
the actual total trap concentration \(N_i^*(x)\) [cf., Eq. (5)],
then \(N_i^*(x^*)\) can be written as \(N_i^*(x^*) + N_i^{[0]*}(x^*)\),
where \(N_i^*(x^*)\) and \(N_i^{[0]*}(x^*)\) are the measured ionized and
neutral trap concentrations, respectively. For shallow traps,
the ionized trap concentration is equal to the total trap concen-
tration, and Eq. (12) becomes

\[
\sigma_t = \pm \int N_i^*(x^*) dx^*
\]

\[
= \pm \int N_i(x) dx = \sigma_{ik}.
\]

Therefore, for shallow traps, Eq. (2) gives the exact trap
density \(\sigma_t\) as concluded earlier.\textsuperscript{10}

It is important to note, however, that the diffusion po-

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tential calculated from Eq. (3) deviates from the exact value \([V_D(0)]\) since it neglects the last two terms on the right side of Eq. (11), which are the contributions to the total diffusion potential due to interface traps. We need to subtract this effect from \(V_D\) to obtain the diffusion potential which is due only to the heterointerface dipole, and thus obtain \(V_D(0)\). This last value then yields the correct value of \(\Delta E_c\) via Eq. (4).

If \(N_\text{to}(x)\) is uniformly distributed between \(x_j\) and \(x_j + d\), Eq. (11) can be simplified to give

\[
V_D(0) = V_{DK} + q\sigma_d d / 2x + q\Delta x_j \sigma_r / \kappa.
\]

(14)

Note that \(V_D(0)\) approaches \(V_{DK}\) as \(d\) or \(\sigma_r\) is decreased. Thus, measurements of \(\Delta E_c\) using the C-V depletion technique are only accurate in the absence of interface traps, although the effects of traps are small for very abrupt HJs.

Note also that an accurate determination of the interface \(\delta V\), although the effects of traps are small for very abrupt HJs. Thus, measurements of \(\delta V\) can be simplified to give

\[
\delta V = \frac{q\Delta x_j \sigma_r}{\kappa}.
\]

As a specific example illustrative of the effects of traps, we model \(n_{0,53}\), \(Ga_{0,47}\)As/InP HJs using materials parameters given in Table I. In this work, several assumptions were made to simplify the numerical simulations: (i) The total trap concentration \(N_\text{to}\) is assumed to be uniformly distributed within a thin region of width \(d\) located on one side of the HJ; (ii) one trap at energy \(E_t\) was assumed for deep interface traps; and (iii) the quasi-Fermi level is assumed to be flat throughout the HJ region. No compositional or doping concentration gradients, image charge or quantum effects in the accumulation region are considered.

Figure 2(a) shows the calculated \(n^*(x^*)\) profiles of an \(n_{0,53}\), \(Ga_{0,47}\)As/InP HJ with various values of \(\sigma_r\), located within 100 Å of the InP side of the HJ. For \(\sigma_r < 0\), electrons are repelled from both sides of the HJ, and thus the peak of \(n^*(x^*)\) decreases while \(x_j^*\) shifts toward the surface \((x = 0)\). When \(\sigma_r = -2 \times 10^{11} \text{ cm}^{-2}\), the peak vanishes completely due to depletion of carriers from both sides of the HJ. This is the so-called "double-depletion" characteristic sometimes observed for HJs with a high density of interface charge.\(^{24,26}\) Positive trapped charge, however, attracts electrons to both sides of the HJ. In this case, the peak becomes higher, and \(x_j^*\) shifts toward \(x_j\).

Figure 2(b) shows the dependence of \(\Delta x_j = x_j - x_j^*\) on interface charge density and conduction band discontinuity energy with two different background doping concentrations. From this figure, we note that for \(\sigma_r > 0\), \(\Delta x_j\) is very small, independent of background doping. However, for acceptor traps where \(\sigma_r < 0\), \(\Delta x_j\) is an increasing function of the trap density. Hence, for these traps, the contribution to \(V_D(0)\) due to the shift in apparent HJ position must be taken into account. Indeed, Fig. 2(b) can be used to estimate the value of \(\Delta x_j\) to use in Eq. (14) given a background carrier concentration, \(N_D\), \(\sigma_r\), and \(\Delta E_{ck}\) as obtained from Eqs. (1)–(3).

To estimate the dependence of the measured conduction

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**Table I. Parameters used for \(n_{0,53}\), \(Ga_{0,47}\)As/InP heterojunction calculations.**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{ck})</td>
<td>eV</td>
<td>0.75</td>
</tr>
<tr>
<td>(E_{hi})</td>
<td>eV</td>
<td>1.35</td>
</tr>
<tr>
<td>(m_i^*)</td>
<td>(m_0^*)</td>
<td>0.04</td>
</tr>
<tr>
<td>(m_i^*)</td>
<td>(m_0^*)</td>
<td>0.07</td>
</tr>
<tr>
<td>(\Delta E_c)</td>
<td>eV</td>
<td>0.24</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>(\text{pF/cm})</td>
<td>1.06</td>
</tr>
<tr>
<td>(x_j)</td>
<td>Å</td>
<td>2500</td>
</tr>
<tr>
<td>(d)</td>
<td>Å</td>
<td>100</td>
</tr>
<tr>
<td>(\delta V)</td>
<td>eV</td>
<td>0.4</td>
</tr>
<tr>
<td>(N_{D1})</td>
<td>(\text{cm}^{-3})</td>
<td>(2 \times 10^{16})</td>
</tr>
<tr>
<td>(N_{D2})</td>
<td>(\text{cm}^{-3})</td>
<td>(2 \times 10^{16})</td>
</tr>
</tbody>
</table>

* Subscripts 1 and 2 refer to \(n_{0,53}\), \(Ga_{0,47}\)As and InP, respectively.

* \(m_0^*\) refers to units of free electron mass.

* Schottky barrier energy.

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band discontinuity on defect charge density, in Fig. 3 we plot 
\((\Delta E_c)_{\text{meas}}\) [calculated using Eqs. (3) and (14)] vs \(\sigma\), with 
\(\Delta E_c = 0.24\) and 0.12 eV. The curves labeled \(\Delta E_{c1}\) corre-
respond to calculations where we take \(\Delta x = 0\) [in Eq. (14)], 
the curves labeled \(\Delta E_{c2}\) give the exact value which is obtained 
using all terms in Eq. (14), while \(\Delta E_{cK}\) is the uncorrected 
value obtained using Eqs. (3) and (4). Observe that \(\Delta E_{c1}\) and 
\(\Delta E_{cK}\) deviate more from the exact value of \(\Delta E_c\) as |\(\sigma|\) 
increases. As shown in Fig. 2(b), \(\Delta x\) is larger for \(\sigma > 0\), and 
thus the deviation of \(\Delta E_{c1}\) is also larger than for positive \(\sigma\).

Furthermore, as \(\Delta E_c\) decreases, the percentage of the devi-
ation of the measured from the actual value of \(\Delta E_c\) increases.
For example, with \(\sigma_r = -5 \times 10^{10} \text{ cm}^2\), \(\Delta E_{c1}\) is greater 
than \(\Delta E_c = 0.24\) eV by 8%, and is greater by 16% for 
\(\Delta E_c = 0.12\) eV. The deviation of \(\Delta E_{cK}\) is twice these values 
for the same range of \(\Delta E_c\).

**B. Deep interface traps**

Significant errors in the determination of the trapped charge 
density, and hence \(\Delta E_c\), can be introduced if deep 
interface traps exist whose occupancy changes during the 
course of the \(C-V\) measurement. During \(C-V\) measurement, 
most of the trapped electrons are emitted as the reverse bias 
is made sufficiently large. Thus, in the limit of large reverse 
bias \(\sigma_{R} \rightarrow \sigma\), for deep donor traps, which is identical to 
the case for shallow traps [cf., Eq. (13)]. Similarly, it can be 
shown (Appendix A) that \(\sigma_{R} \rightarrow -\sigma\) for acceptor traps, 
leading to discrepancies between the measured and actual 
values of interface trap densities.

Due to the relatively long time response of deep traps, it is 
necessary to consider their dynamical nature to under-
stand the measured \(C-V\) data. The emission rate of charge 
from the traps is given by 
\[
\frac{e_a}{g_{ac}(u)}(u)N_e \exp(-E_a/k_BT),
\]
where \(\sigma_{ac}\) is the trap capture section, \(u\) the mean thermal 
velocity of electrons, and \(N_e\) is the effective conduction band 
density of states. If the ac capacitance measurement frequen-
cy is \(\omega \ll \varepsilon_a\), the measurement is defined as low frequency 
(LF), and if \(\omega \gg \varepsilon_a\), it is referred to as a high frequency 
(HF) measurement. According to Eq. (15), the emission rate can 
be decreased by lowering the sample temperature \(T\). Hence, 
a low frequency measurement may become a high 
frequency measurement by lowering \(T\). Since the number of 
trapped electrons which are able to respond to the ac modu-
lation signal decreases as frequency is increased, the result-
tant apparent profile \([n^*(x^*)]\) is distorted by changing ei-
ther temperature or frequency, which ultimately affects the 
value obtained for \(V_{DK}\).

The frequency dependence of the capacitance for homo-
junctions with deep traps has been studied previously.\(^{27-29}\)
Both the rate equation and Poisson's equation have to be 
solved simultaneously to obtain the frequency-dependent 
junction capacitance. In general, this makes the expression 
for the high frequency capacitance \(C_{HF}\) very complicated.
In order to simplify the case of traps localized at a HJ, Kaz-
mierski \etal.\(^{16}\) proposed a model which assumes that the 
occupancy of the traps is unchanged under small increments 
in the ac modulation voltage \((dV)\). The occupancy of traps at 
\(V\) at HF is, therefore, the same as at \(V - dV\). Further-
more, it was assumed that the sweep frequency of the reverse 
bias \((\Omega)\) is always \(\Omega < \varepsilon_a\), i.e., the trap occupancy is always 
in equilibrium with the "dc" voltage increment \((dV)\).
Therefore, this approach is valid for \(\Omega \ll \varepsilon_a\).

Another, somewhat different model proposed by Jeong 
\etal.\(^{21}\) was used to explain dependence of the \(n^*(x^*)\) profile 
of InGaAs/GaAs HJs on temperature. The expression used 
to describe the occupancy traps [Eq. (10) in Ref. 21] is a 
function of \(\varepsilon_a\). It can be shown (Appendix B) that this 
model is only valid when \(\varepsilon_a = \Omega\). Both the results of Kazmierski 
and Jeong are, therefore, applicable to different frequency 
regimes. In Appendix B, we derive a single result which is 
valid for all \(\Omega < \varepsilon_a\). In practice, we can arrange the experi-
ment such that \(\Omega \ll \varepsilon_a\), in which case the results of Kaz-
mierski are accurate, and hence, will be followed in the re-
mainder of this section.

Figure 4 shows the apparent carrier concentration pro-
files for an In$_{0.53}$Ga$_{0.47}$As/InP HJ with a deep acceptor den-
sity \(\sigma_r = -1 \times 10^{11} \text{ cm}^{-2}\) calculated for both LF (solid 
line) and HF (dashed line) measurements. The energy of 
the trap from the InP conduction band minimum is 0.25 eV.
Note that only one peak is observed for \(\Delta E_c = \varepsilon_a\). This is 
different from the case treated by Jeong\(^{21}\) where two peaks 
were observed: one due to electron accumulation and the 
other due to traps. However, we consider the case of 
\(\Delta E_c = \varepsilon_a\), since it has been observed experimentally for this 
HJ system in the present, and in previous work.\(^{9,15,17}\)
The double-depletion characteristic of the apparent profile 
observed for the same shallow interface trap density [cf., Fig. 
2(a)] disappears completely for both profiles. This difference 
is due to the emission of electrons from the deep traps 
during the course of the \(C-V\) measurement, whereas the 
charge state of shallow traps remains constant. Note also 
that \(V_{DK}\) [Eq. (3)] is reduced for the high frequency 
measurement. For the data shown, \(V_{DK}\) is found to equal 0.25 
and 0.21 eV at low and high measurement frequency, respec-
tively.
The measured trap densities \(\sigma_n\) were calculated for these profiles. As expected, \(\sigma_n\) is equal to \(\sigma\), for deep donors at all frequencies. On the other hand, for deep acceptor traps, \(\sigma_k\) is nearly independent of \(\sigma\), and is approximately equal to zero in both the HF and LF regimes. This result is consistent with theory, as discussed at the beginning of this section, and in Appendix A.

Figure 5 is a plot of \(\Delta E_c\) as a function of trap density. Both low frequency (LF) and high frequency (HF) cases are considered. For deep acceptor traps, \(\Delta E_c\) is nearly constant \((-0.24\,\text{eV})\) at low frequency over the entire range of \(\sigma\), considered, and is close to the actual value \((\Delta E_c(0))\). This implies that the energy bands are less distorted by deep rather than shallow traps (cf., Fig. 3). This results since deep traps can emit charge during the course of the C-V measurement, which reduces their contribution to the diffusion potential. At high frequency, \(\Delta E_c\) drops to 0.20 eV as \(\sigma\) increases to \(-1 \times 10^{11}\,\text{cm}^{-2}\).

Errors in measuring \(\Delta E_c\) are also present for deep donor traps. Although \(\Delta E_{ck}\) measured at LF is close to the exact value, in the HF regime large errors are incurred. For example, at \(\sigma = 1 \times 10^{10}\,\text{cm}^{-2}\), \(\Delta E_{ck} = 0.6 \Delta E_c(0)\). This tendency appears to explain the often observed frequency dependence of \(\Delta E_c\) obtained by C-V techniques,\(^{14-17}\) with the most accurate values of \(\Delta E_c\) obtained at low frequency (or alternatively high temperature).

Figure 6 is a plot of \(\Delta E_{ck}\) versus temperature \((T)\) assuming a donor trap density of \(\sigma = 1 \times 10^{11}\,\text{cm}^{-2}\). Note that \(\Delta E_{ck}\) gradually drops with temperature, with the HF data being somewhat more temperature dependent. At 130 K, \(\Delta E_{ck} = 0.075\,\text{eV}\) at HF, which is well below the exact value of 0.24 eV. As implied by the discussion above, there should exist a transition temperature \((T_c)\) below which the value of \(\Delta E_{ck}\) drops from the LF to the HF curve. The transition occurs when \(e_e(T_c) = \omega\). The effect shown in Fig. 6 clearly explains the apparent dramatic drop of the measured conduction band discontinuity \((\Delta E_{ck})\) to nearly zero at \(T=150\,\text{K}\), which was observed by Forrest et al.\(^{14}\) for In_{0.53}Ga_{0.47}As/InP HJs.

The temperature dependence for acceptor traps was similarly explored. We found that, as for donor traps \(\Delta E_{ck}\) drops with temperature, although the drop in the case of acceptors is not as severe as for donor traps (cf., Fig. 5). Indeed, the very strong dependence found for In_{0.53}Ga_{0.47}As/InP HJs is evidence that the effect is due to donor traps, contrary to conclusions made in previous work on this subject.\(^{14-17}\)

III. CALCULATION OF \(\Delta E_c\) USING THE EMENDED EQUATIONS

As mentioned above, Eq. (11) or (A4) can be used to correct the value of the measured diffusion potential \((V_{dk})\) in the presence of deep traps. However, the correction term involves the ionized trap concentration profile \([N_+(x^*)]\) for donors, or the neutral trap profile \([N_0(x^*)]\) for acceptors. Unfortunately, these are not easy to extract directly from the free carrier concentration profiles.

As shown in Eq. (5), the ionized trap concentration

![FIG. 4. Apparent free carrier concentration profile of deep acceptor traps at low frequency (solid line) and at high frequency (dashed line). The trap density \(\sigma\), acceptor energy depth \(E_a\), and conduction band discontinuity \(\Delta E_c\) are assumed to be \(-1 \times 10^{11}\,\text{cm}^{-2}\), 0.25 eV, and 0.24 eV, respectively.](image)

![FIG. 5. Calculated conduction band discontinuity energy \(\Delta E_{ck}\) vs the trap density \(\sigma\) at low and high frequency for both deep acceptor and donor traps.](image)

![FIG. 6. Calculated conduction band discontinuity \(\Delta E_{ck}\) vs temperature \((T)\) for deep donor traps. The transition temperature \((T_c)\) is shown at \(T=210\,\text{K}\).](image)
$N_i(x)$ is a function of bias due to the dependence of $E_c(x)$ on $V$. Figure 7 shows how the apparent trap concentration profile $[N_i^*(x*)]$ is related to the actual ionized trap concentration $[N_i(x)]$ at different voltages for donor traps. In the figure, $\sigma_i = 1 \times 10^{11}$ cm$^{-2}$, $T = 130$ K, and $E_i = 0.25$ eV are assumed. Also, the trap region is taken to be 100 Å wide centered at 2550 Å, and the HJ is at $x_2 = 2500$ Å. Figure 7(a) shows the occupancy of the traps at different reverse bias voltages. Apparently, the ionized trap concentration at each position increases as the voltage increases, finally becoming fully ionized at $V > 2.4$ V. In Fig. 7(b) we plot $\Delta N_i(x)$ vs $V$. Here, $\Delta N_i(x)$ is the change of occupancy in $N_i(x)$ obtained by increasing the reverse bias voltage by $DV$ ($= 0.06$ V in this figure). The area under each curve (shaded for 1.20 V) is the number electrons emitted from the traps per unit area when the voltage is increased by $DV$. The charge distribution ionized by a small change $DV$ in the voltage, $[\Delta N_i(x)]$ should be equal to the area of the corresponding strip of $N_i^*(x*)$ between $x^*$ and $x^* + dx$ which are evaluated at $V$ and $V + DV$, respectively [Fig. 7(c)]. Therefore, for donorlike traps, we conclude that

$$N_i^*(x*)dx^* = \int_{x_j}^{x_j+dv} \Delta N_i(x)dx. \quad (16a)$$

Similarly, for acceptor traps with neutral trap density $N^{(10)}_i(x*)$, we have

$$N^{(10)}_i(x*)dx^* = -\int_{x_j}^{x_j+dv} \Delta N_i(x)dx. \quad (16b)$$

Figure 8 shows the apparent free carrier concentration profiles $[n^*(x*)]$ in the presence of acceptor traps. The apparent trap profiles $[N^{(10)}_i(x*)]$ are also shown. These latter profiles are obtained by the procedure discussed with respect to Fig. 7. As implied earlier, the areas under the $N^{(10)}_i(x*)$ profiles are equal to the actual trap density in both frequency regimes. Furthermore, the exact value of $\Delta E_i (=0.24$ eV) is recovered after correcting $\Delta E_{r,k}$ using Eq. (A4) for acceptor traps.

It should be noted, however, that making such a correction to $\Delta E_{r,k}$ using the integrals over the apparent trap distribution as in Eqs. (11) or (A4) is not useful since we need to be able to generate (by computer simulation) $n^*(x*)$ to obtain $N_i^*(x*)$. Once we have generated $n^*(x*)$, we will have already obtained $\Delta E_i$ without the need for Eq. (11). Thus, in general, the emended forms of Eq. (3) as given by Eq. (14) are more often useful, providing that an estimate of $d$ can be obtained. Typically, $d$ can range from a few atomic layers for molecular beam epitaxially grown samples, to a few hundred angstroms for samples grown by liquid phase epitaxy (LPE). This distance can be independently obtained by Auger electron spectroscopy or several other direct microscopic techniques. Thus, to obtain $V_{r,k}(0)$, the $n^*(x*)$ profile can be determined to good accuracy at LF (see Sec. II), thereby obtaining $\sigma_i = \sigma_{r,k}$ using Eq. (2). From these results, $\Delta E_i$ can be approximately obtained from Fig. 2(b), and using the estimate of $d$ consistent with the growth processes employed, $V_{r,k}$ is easily corrected to give $V_{r,k}(0)$ using Eq. (14). This procedure is employed in Sec. IV for In$_{0.53}$Ga$_{0.47}$As/InP HJs. One should keep in mind that such

![Diagram](image-url)
a procedure can correct the value of $\Delta E_{ck}$ by 10%-50%. However, if $\sigma_t > 10^{11}$ cm$^2$, the correction terms in Eq. (14) become comparable to $V_{DK}$. In this case, the values of $V_D(0)$ and $V_{DK}$ should both be viewed with caution since under these conditions, the energy bands at the heterojunction are predominantly influenced by the trapped charge rather than the HJ dipole potential.

IV. EXPERIMENTAL RESULTS

Two In$_{0.33}$Ga$_{0.67}$As/InP HJ samples were investigated to test the results of Secs. II and III. Sample No. 1 was a mesa-type structure consisting of layers of adventitiously doped n-InP and n-In$_{0.33}$Ga$_{0.67}$As successively grown by LPE on a (100) p-InP substrate with a Zn doping of $N_A = 6.5 \times 10^{16}$ cm$^{-3}$. The n-InP layer was 3 $\mu$m thick, and the free carrier concentration of both n-type layers was $4 \times 10^{15}$ cm$^{-3}$. The lattice mismatch of the layers is 0.08%. Details of the fabrication and growth processes for this sample have been published previously.$^{14}$

For sample No. 2, approximately 2.0 $\mu$m of n-In$_{0.33}$Ga$_{0.67}$As with a carrier concentration of $2 \times 10^{15}$ cm$^{-3}$ was grown via LPE onto a 2.0-$\mu$m-thick n-InP layer, also with a carrier density of $2 \times 10^{15}$ cm$^{-3}$. Lattice mismatch between the layers was less than 0.01%. In this case, the substrate was (100) sulfur-doped, n$^+$-InP with a carrier concentration $> 2 \times 10^{18}$ cm$^{-3}$. A rectifying organic-on-inorganic (OI) semiconductor contact was then formed on In$_{0.33}$Ga$_{0.67}$As side using the organic compound 3, 4, 9, 10-perylenetetracarboxylic dianhydride (PTCDA).$^{30}$ Details of OI diode fabrication have also been presented previously.$^{31,32}$ Due to the large energy barrier at the OI/In$_{0.33}$Ga$_{0.67}$As contact, the diode has a small reverse leak current, and can be depleted far from the surface before breakdown. This allows one to quickly and easily obtain the free carrier concentration profiles.

For sample No. 1, there is a dramatic drop$^{14}$ of $\Delta E_{ck}$ as $T$ is decreased from 170 to 135 K using a measurement frequency of 1 MHz. This implies that the transition from the LF to HF regime (Fig. 6) occurs at $T_c = 150$ K at this measurement frequency. Thus, data at $T = 201$ K (Fig. 9(a)) are obtained at LF, while those taken at $T = 102$ K (Fig. 9(b)) corresponds to the HF regime.

Figure 9 also shows the computer simulated $n^*(x*)$ profiles at $T = 201$ and 102 K. We obtain the best fit by assuming $d = 200$ A, $x_j = 3$ $\mu$m, $\Delta E_i = 0.22$ eV, $\sigma_i = 3 \times 10^{10}$ cm$^{-2}$, and a donor trap at energy $E_i = 0.17$ eV. Here, $d$ is inferred from optical response time measurements made for these HJ diodes.$^{33}$ These data are consistent with those reported earlier$^{14}$ [where $E_i = 0.20 \pm 0.02$ eV, $\sigma_i = (3.0 \pm 0.5) \times 10^{10}$ cm$^{-2}$]. The difference in $\Delta E_i$ between the measured ($\Delta E_{ck} = 0.20$ eV) and the best fit value obtained from the simulated $n^*(x*)$ profile arises from positive interface charges near the HJ. Note that the fit at both low and high temperature is in reasonable agreement with the data, although the peak heights differ by a factor of 2. This discrepancy appears to arise from the resolution limit of the capacitance measurement. For example, the value of $dC/dV$ at the $n^*(x*)$ peak is equal to 0.03 pF/V. On the other hand, the value of $dC/dV$ for the simulation result is 0.015 pF/V. Another error source may arise from compositional grading in the transition region between In$_{0.33}$Ga$_{0.67}$As and InP which would tend to lower the measured peak due to a spatial broadening of the charge.

If Eq. (14) is used to correct the value of $\Delta E_{cr}$ by assuming $d = 200$ A, $x_j = 400$ A, and $\sigma_i = 3 \times 10^{10}$ cm$^{-2}$, the exact value of $\Delta E_r(0)$ is also found to be equal to 0.22
eV. This is consistent with the value obtained from the best fit of the experimental data and those obtained independently in other experiments.15-18,31 Note also that the deep trap is assumed to be located on the InP site of the HJ. If a deep level with \( E_t = 0.17 \) eV is assumed to be located on the In\(_{0.53}\)Ga\(_{0.47}\)As side, the accumulation electron peak and the deep trap peaks become separated as in Fig. 8. This differs with recent conclusions of Kazmerski et al.16 regarding the origins of this trap.

A considerably different situation exists for sample No. 2, as shown in Fig. 10. At \( T = 300 \) K, the profile has two peaks, unlike the typical peak-valley profile shown in Fig. 2(a). According to simulation results for this HJ (taking \( \Delta E_c = 0.24 \) eV), the electron concentration due to accumulation at the HJ dipole should be \( \sim 1 \times 10^{16} \) cm\(^{-3}\) at room temperature—a value which is too small to account for the observed peak heights of \( \sim 2 \times 10^{17} \) cm\(^{-3}\). Furthermore, as the temperature decreases to 270 K, both peaks A and B shift dramatically toward the InP side. These peaks can be explained as due to emission of charge from deep traps at the HJ.

Since the peak due to a trap is shifted further toward the substrate with increasing \( E_t \), we expect that peak B is at larger \( E_t \) than peak A. Also note that both peak heights increase at lower temperature (270 K). A fit to the data at \( T = 270 \) K consistent with these assumptions is shown by the dashed line. Parameters used in the fit are given in Table II.

As the temperature decreases from 270 to 230 K, both peaks decrease in amplitude and move further toward the substrate. Peak B decreases continuously and finally disappears at \( T = 150 \) K. This indicates that, at low temperature, traps responsible for peak B are in the HF regime with a measurement frequency of 1 MHz (cf., Fig. 8). On the other hand peak A (with smaller \( E_t \)) has a higher emission rate (or lower transition temperature \( T_e \)). Since the height of peak A at \( T = 150 \) K is larger than at room temperature, this implies that \( T_e \) must be lower than 150 K.

When the temperature decreases from 230 to 200 K, a third peak (C) appears. The position of peak C is independent of temperature from 200 to 150 K. Furthermore, the carrier concentration of this peak is \( \sim 2 \times 10^{16} \) cm\(^{-3}\) at \( T = 150 \) K, which is close to the expected value \( (1.6 \times 10^{16} \) cm\(^{-3}\) for the HJ accumulation electron concentration assuming \( \Delta E_c = 0.24 \) and \( N_p = 2 \times 10^{15} \) cm\(^{-3}\)). Therefore, peak C is attributed to accumulation of electrons due to the intrinsic heterojunction dipole potential.

From the data, we obtain \( \sigma_p \sim 7 \times 10^{11} \) cm\(^2\) for both peaks A and B, which is an anomalously high trap density. We speculate that these two deep traps are, therefore, due to extrinsic impurities or defects (e.g., anion vacancies) incurred during growth, although their source is not fully understood at present. Since \( \sigma_p > 0 \), the defects appear to be donors as in the case of sample No. 1, rather than acceptor-like as suggested previously.14,15,17 Due to the large differences in \( \sigma_p \) for samples 1 and 2, it is not clear whether one or both peaks have the same origins for the two samples, although in both cases the peaks are due to a high density of donors. However, contrary to previous speculations on this matter, it is not due to lattice mismatch between layers. For sample No. 2, the mismatch is only 0.01% which could account for \( \sigma_p \leq 10^7 \) cm\(^{-2}\). Further, the lattice mismatch for sample No. 2 is less than for sample No. 1, although the measured \( \sigma_p \) is greater for the former sample.

V. CONCLUSIONS

The accuracy of the widely used C-V technique proposed by Kroemer et al.18 for the measurement of band-edge discontinuity energies has been investigated. Emended equations for determination of the trap density (\( \sigma_p \)) and conduction band discontinuity energy (\( \Delta E_c \)) in the presence of both deep and shallow traps have been derived. The accuracy for determining the conduction band discontinuity ener-

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**Table II. The parameters used in fitting data obtained for sample No. 2.**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{t1} )</td>
<td>eV</td>
<td>0.03</td>
</tr>
<tr>
<td>( E_{t2} )</td>
<td>eV</td>
<td>0.21</td>
</tr>
<tr>
<td>( N_{t1} )</td>
<td>cm(^{-1})</td>
<td>( 3 \times 10^{17} )</td>
</tr>
<tr>
<td>( N_{t2} )</td>
<td>cm(^{-1})</td>
<td>( 2 \times 10^{17} )</td>
</tr>
<tr>
<td>( d )</td>
<td>Å</td>
<td>200</td>
</tr>
<tr>
<td>( \Delta E_c )</td>
<td>eV</td>
<td>0.24</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>cm(^{-1})</td>
<td>1.95</td>
</tr>
<tr>
<td>( N_p )</td>
<td>cm(^{-3})</td>
<td>( 2 \times 10^{15} )</td>
</tr>
</tbody>
</table>

*Subscripts 1 and 2 refer to In\(_{0.53}\)Ga\(_{0.47}\)As and InP, respectively.

* \( E_t \) is trap energy depth from In\(_{0.53}\)Ga\(_{0.47}\)As and InP, respectively.

* \( N_p \) is integrated trap density = \( \sigma_p / d \).
ergy can be improved by correcting the measured value according to these new expressions.

We have also shown that the magnitude of the discrepancy between $\Delta E_c$ and measurement is dependent on both temperature and measurement frequency. The difference between the measured conduction band discontinuity ($\Delta E_{ck}$) and the actual value ($\Delta E_c(0)$) becomes large at low temperature, high measurement frequency, or for deep traps. From computer simulations of C-V measurements, we can explain the dramatic drop of $\Delta E_c$ to zero at low temperature observed previously$^{14-17}$ for In$_{0.33}$Ga$_{0.67}$As/InP HJs as due to traps localized at the heterointerface.

The theoretical and experimental free carrier concentration profiles measured at low and high temperature for In$_{0.33}$Ga$_{0.67}$As/InP HJs were studied. We correct the measured conduction band discontinuity energy ($\Delta E_{ck}$) by applying the emended equations to the C-V data at $T = 201$ K. The value of $\Delta E_c$ obtained using this technique is 0.22 eV, consistent with values obtained by other workers, as well as by numerical simulations. The temperature-dependent apparent profiles for a second sample show the existence of two deep levels. The source of these defects, however, is not fully understood at present. Other experiments (e.g., DLTS, admittance spectroscopy) have to be used to obtain more detailed information.

In summary, the use of the emended equations is straightforward and should lead to more accurate determination of $\Delta E_c$ measured in the presence of interfacial defects than has been possible using standard C-V techniques. Finally, the results presented in this work provide a means for understanding many complex phenomena which are observed in the course of HJ profiling using C-V data.

ACKNOWLEDGMENTS

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APPENDIX A: TRAP CHARGE DENSITY AND CONDUCTION BAND DISCONTINUITY FOR DEEP ACCEPTOR TRAPS

If the reverse bias is made large enough, most of the electrons in the traps are emitted, and the traps become neutral with density, $N_i^{(0)}(x^*)$. Thus,

$$- \int_{-\infty}^{x} N_i^{(0)}(x^*) dx^* \rightarrow \sigma_i.$$  

In substituting $N_i^*(x^*)$ with $N_i^*(x^*) - N_i^{(0)}(x^*)$, Eq. (12) becomes

$$\sigma_{ik} = - \int_{-\infty}^{x} N_i^*(x^*) dx^* \rightarrow \sigma_i + \int_{-\infty}^{x} N_i^{(0)}(x^*) dx^*. \quad (A1)$$

Comparing the above equations, we conclude that $\sigma_{ik} \rightarrow 0$ for acceptor-like traps.

For calculating the diffusion potential, $N_i^*(x^*)$ in Eq. (11) should also be replaced with $N_i^*(x^*) - N_i^{(0)}(x^*)$. Thus, assuming charge conservation:

$$V_D(0) = V_{dk} - q/k \int_{-\infty}^{x} [N_i^*(x^*) - N_i^{(0)}(x^*)] \times (x^*-x_0) dx^*$$

$$= V_{dk} - q/k \int_{-\infty}^{x} N_i^*(x) (x-x_0) dx$$

$$+ q/k \int_{-\infty}^{x} N_i^{(0)}(x^*)(x^*-x_0) dx^*. \quad (A2)$$

If $N_i(x)$ is uniformly distributed between $x_j$ and $x_{j+1}$, Eq. (A2) becomes (for $\sigma_i < 0$)

$$V_D(0) = V_{dk} + \frac{q\sigma_i d}{(2k)} + q/k \int_{-\infty}^{x} N_i^{(0)}(x^*) (x^*-x_0) dx.$$  

$$= V_{dk} + \frac{q\sigma_i d}{(2k)} + \int_{-\infty}^{x} N_i^*(x^*) dx^*. \quad (A3)$$

Note that for shallow acceptor traps, $N_i^{(0)}(x^*)$ is zero since this term represents the total number of neutral traps. In this case, Eq. (A3) can be simplified to yield Eq. (14).

Defining $\Delta x_j$ as the difference between $x_j$ and $x_{j+1}$, Eq. (A3) becomes

$$V_D(0) = V_{dk} + \frac{q\sigma_i d}{(2k)} + \int_{-\infty}^{x} N_i^*(x^*) dx^*.$$  

$$= V_{dk} + \frac{q\sigma_i d}{(2k)} + \int_{-\infty}^{x} N_i^*(x^*) dx^*.$$  

Note also that the fourth term approaches zero for acceptor traps since all of the electrons in the traps are emitted during the C-V measurement.

APPENDIX B: FREQUENCY DEPENDENCE OF THE C-V DATA

In this Appendix, the HF models proposed by Kazmerski et al.$^{16}$ and Jeong et al.$^{21}$ are recast into a single expression. The rate equation describing electron capture at a defect can be written as

$$\frac{\partial N_i}{\partial t} = N_i [c_e n (1-f_2) + c_p (1-f_1) - e_2 f_1 - c_p p f_2], \quad (B1)$$

where $f_2$ is the occupancy of the trap, $n(p)$ is the free electron (hole) concentration, $c_e (c_p)$ is the electron (hole) capture coefficient, and $e_2 (e_p)$ is the electron (hole) emission rate.

Applying an ac modulation signal, all the variables will have small variations about their steady-state values, viz.: $p = p_0 + \delta p$, $n = n_0 + \delta n$, and $N_i = N_i(0) + \delta N_i$. Here $N_i(0)$ is the number of ionized traps at $t = 0$. If only first-order terms are retained, Eq. (B1) becomes

$$\frac{\partial \delta N_i}{\partial t} = - \frac{\partial N_i}{\tau}, \quad (B2)$$

where

$$\tau = 1/[c_e (n_0 + n_1) + c_p (p_0 + p_1)]$$

is the trap time constant and $n_i (p_i)$ is the electron (hole) density if $E_F = E_v$.

If the traps are located in the depletion region ($n_b - 0$), and the interaction with the valence band is ignored for $n$-
type material (where \( \rho \ll n_i \)) the trap time constant can be simplified to

\[
\tau = \frac{1}{c_n n_i} = \frac{1}{[\sigma_{\omega}(\nu) N_e \exp(-E_i/k_BT)]} = \frac{1}{e_n}
\]

[cf. Eq. (15)].

The solution of Eq. (B2) can then be written as

\[
N_x(t) = N_x(0) + \{N_x(\infty) - N_x(0)\} (1 - e^{-t/\tau}).
\]

(B3)

Case 1: Bias sweep frequency small (\( \Omega \ll \omega \))

Assume at \( t = 0 \) that a reverse bias voltage \( V \) is applied to the sample. At \( t = t_i \), the voltage increases to \( V + dV \), where \( dV \) is the ac modulation signal. If the trap concentration is a function of position, \( N_x(t) \) becomes \( N_x(x, t) \) and Eq. (B3) becomes

\[
N_x(x, V + dV) = N_{x_{0}} + \{N_x(\infty) - N_{x_{0}}\} \left[ 1 - \exp\left( -t_i/\tau \right) \right].
\]

(B4)

Note that \( N_x(0) \) has been replaced with \( N_{x_{0}} \), since the trap charge (or discharge) of the traps can respond to the sweep frequency (\( \Omega \)) of the dc bias. From this same argument, \( N_x(\infty) \) can be replaced by \( N_{x_{0}} \). Furthermore, as \( t_i/\tau \to 0 \), \( N_x(x, V + dV) \to N_{x_{0}} \). This is just the approach used by Kazmierski et al.\(^{10}\)

Case 2: Bias sweep frequency large (\( \omega \ll \Omega \))

If the temperature is low enough such that \( \omega \ll \Omega \), the boundary condition \( N_x(0) = N_{x_{0}} = f_{x}(x, V) \) is no longer valid since the occupancy of electrons cannot follow the sweep frequency (\( \Omega \)) of dc reverse bias \( V \). As a boundary condition, assume that all the traps are occupied by electrons at \( V = 0 \) at \( t = 0 \) [i.e., \( N_x(0) = N_{x_{0}} \)]. On the other hand, as \( t \to \infty \), \( N_x(\infty) \) should be \( N_{x_{0}} \). If voltage \( V + dV \) is applied at \( t = \pi/\omega \) (half the period of ac small signal), Eq. (B3) becomes

\[
N_x(x, V + dV) = N_{x_{0}} - N_{x_{0}} \left[ 1 - f_{x}(x, V + dV) \right] \left[ 1 - e^{-\pi/\omega} \right].
\]

(B5)

Equation (B4) is the HF model proposed by Jeong et al.\(^{21}\)

In conclusion, Eq. (B3) is the rigorous solution of which the previous treatments are special cases. However, the regime treated by Jeong is not practical and hence should not lead to correct results when applied to most experimental data. On the other hand, the approach of Kazmierski is valid to good approximation in most cases.

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\(^{15}\) M. Ogura, M. Mizuta, and K. Oraka, J. Appl. Phys. 52, 1502 (1982).


Accurate determination of heterojunction band discontinuities in the presence of interface traps using capacitance-voltage techniques

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The effects that interface traps have on the determination of the heterojunction band discontinuity energies \( \Delta E \) measured via capacitance-voltage analysis are considered. We show that both the trap density \( \sigma_{\text{K}} \) and conduction-band discontinuity energy \( \Delta E_{\text{CK}} \) measured using the method of Kroemer, Chien, Harris, and Edwall [Appl. Phys. Lett. 36, 295 (1980)] are functions of the heterointerface width \( d \), the difference between the actual and the measured heterojunction positions \( \Delta x \), and the doping levels of the two contacting materials. These error sources can be corrected by using simple amended equations developed in this study.

This amended technique improves the measurement accuracy of both trap density and heterojunction band discontinuity energy, is easy to use, and is relatively insensitive to variations in doping and trap density in the interface region. This technique is applied to the analysis of a vapor phase epitaxial N-n InP/InAs/GaAs heterojunction for which we find \( \Delta E = (0.24 \pm 0.01) \, \text{eV} \).

I. INTRODUCTION

The capacitance-voltage (C-V) technique proposed by Kroemer et al.\textsuperscript{1} has been widely used to measure the energy band discontinuities of many isotype heterojunctions (HJs).\textsuperscript{1-5} This method exhibits features which have advantages over many other techniques used in determining HJ band discontinuity energies. For example, the measurements are not sensitive to compositional gradients\textsuperscript{6} in the heterointerface region, and are relatively insensitive to materials parameters such as effective mass and permittivity.\textsuperscript{7} By comparison, photoluminescence spectroscopy of multiple quantum wells is strongly dependent on an accurate knowledge of effective mass, quantum-well width, and well profile.\textsuperscript{8} Likewise, x-ray photoelectron spectroscopy\textsuperscript{9} is subject to errors due to the need of subtracting large valence-bond energies (\( \sim 10-15 \, \text{eV} \)) to obtain a small discontinuity energy (\( \sim 0.1-0.5 \, \text{eV} \)). Furthermore, current-voltage measurements are vulnerable to errors induced by parasitic current sources.

In addition to determining the band discontinuity energy, the C-V technique is also useful for measuring the density of the shallow trapped charge near the heterojunction. With this information, the relative quality of a HJ can be assessed such that, \textit{a priori}, the accuracy of the subsequent band discontinuity energy measurement can be ascertained.

II. THEORY

The HJ properties are determined by first obtaining the apparent (or measured) free-carrier concentration profile \( n^*(x^*) \) from C-V data. These data result from depleting the HJ by applying reverse voltage to an adjacent rectifying contact. Hence,\textsuperscript{10}

\[
n^*(x^*) = \left( \frac{2}{q\kappa} \right) \frac{dV}{d(1/C^2)},
\]

where \( x^* = \kappa/C \) is the apparent distance from the rectifying contact, \( q \) is the electronic charge, and \( \kappa \) is the permittivity. The density of the shallow trapped interface charge, \( \sigma_{\text{K}} \), and the diffusion potential, \( V_{\text{DK}} \), of an n-type, isotype HJ can then be obtained using\textsuperscript{1}

\[
\sigma_{\text{K}} = - \int_{-\infty}^{\infty} \left[ N_D(x^*) - n^*(x^*) \right] dx^*,
\]

\[
V_{\text{DK}} = \frac{q}{\kappa} \int_{-\infty}^{\infty} \left[ N_D(x^*) - n^*(x^*) \right] (x^* - x^*_i) dx^*,
\]

where \( N_D(x^*) \) is the background donor concentration at the apparent position \( x^* \), and \( x^*_i \) is the apparent position of the HJ as measured from the location of the charge accumulation peak in the carrier concentration profile. The conduction-band discontinuity energy \( \Delta E_{\text{CK}} \) is calculated using the diffusion potential via \( \Delta E_{\text{CK}} = qV_{\text{DK}} + \delta_1 - \delta_1 \), where \( \delta_1 \) and \( \delta_2 \) are the Fermi energies (with respect to the conduction-band minima) in the bulk of the contacting semiconductors. Here, subscripts 1 and 2 refer to the different materials comprising the HJ.

There are several inherent problems with the C-V technique which can lead to systematic errors in determining both \( \Delta E \) and the actual fixed interface charge density, \( \sigma_i \). For example, the use of Eqs. (2) and (3) is based on the assumptions that the apparent HJ position \( (x^*_i) \) is equal to its actual position \( (x_i) \), and that the trap density \( \sigma_{\text{K}} \) is low enough such that it does not significantly perturb the often small intrinsic heterojunction dipole potential. However, due to the limited spatial resolution inherent in C-V data,\textsuperscript{11} \( x_i^* \) is shifted away from \( x_i \), toward the electron accumulation region at the HJ. In order to correct for this effect, Rao et al.\textsuperscript{11} calculated a series of pairs of \( \sigma_{\text{K}} \) and \( \Delta E_{\text{CK}} \) for (Ga,In)P/GaAs HJs by assuming different values of \( x_i \), and then choosing the actual position of the HJ to minimize \( \sigma_{\text{K}} \).

Since this approach assumes that the HJ has a very low density of interface states, it can only be reliably applied to sam-
On the other hand, we can expect that a high density of defects will influence the values obtained for \( V_{Dk} \), particularly if the diffusion potential is small.\(^{12,13} \) This situation is made worse if the doping levels on both sides of the HJ are different. To illustrate this last point, in Fig. 1 we show the calculated apparent free carrier concentration profile of an InP/InGaAs heterojunction with background dopings of \( N_{D1} = 1.1 \times 10^{16} \text{ cm}^{-3} \) and \( N_{D2} = 3 \times 10^{16} \text{ cm}^{-3} \) for InP and In\(_{0.53}\)Ga\(_{0.47}\)As, respectively. The calculation is accomplished by numerically solving Poisson’s equation starting at the rectifying Schottky barrier contact made to the InP layer, and assuming that \( \Delta E_c = -0.24 \text{ eV} \), where the negative sign implies that the conduction-band energy is greater on the InP side than on the InGaAs side of the HJ.\(^{3,14} \) Furthermore, for this calculation we assume that the Schottky barrier height is 0.4 eV and the interface trap density is \( \sigma_i = -5 \times 10^{10} \text{ cm}^{-2} \), which is confined to a region of width \( d = 200 \text{ Å} \) on the InP side of the heterointerface.

In using the C-V depletion technique, the background doping levels of both materials are obtained from the \( n^*(x^*) \) profile at distances \( x^* \) far from either side of the HJ, and the integrals in Eqs. (2) and (3) are then evaluated by assuming that \( N_{D1} \) and \( N_{D2} \) are uniform in the HJ region. An abrupt step in doping between these values is assumed to occur at the HJ whose position is determined from \( x^* \). As can be seen from the cross-hatched box in the figure, the integral in Eq. (2) will be incorrect due to the excess area arising from the difference between \( x^* \) and the actual position \( x_1 \). The error incurred is increased with an increasing difference between \( N_{D1} \) and \( N_{D2} \). We can calculate the magnitude of the error by rewriting Eq. (2) as

\[
\sigma_i = -\int_{x_1}^{x_2} \left[ N_{D1} - n^*(x^*) \right] dx^*
- \int_{x_2}^{x_1} \left[ N_{D1} - n^*(x^*) \right] dx^*
- \int_{x_1}^{s_1} \left[ N_{D2} - n^*(x^*) \right] dx^*
- \int_{s_1}^{s_2} \left[ N_{D2} - n^*(x^*) \right] dx^*,
\]  

(4)

The first and last integrals on the right-hand side of Eq. (4) are just \( \sigma_i \), whereas the middle integrals arise since \( \Delta x_1 = x_1 - x^*_1 \) is not zero. Evaluating these integrals for the profile in Fig. 1 indicates that \( \sigma_i = -5.8 \times 10^9 \text{ cm}^{-2} \), or about an order of magnitude less than the actual value. Hence, these effects cannot be ignored without inducing large errors in the fixed interface charge density as obtained using previous methods.

These errors can be reduced or eliminated by solving the integrals in Eq. (4). Grouping terms we obtain

\[
\sigma_i = \sigma_{iK} - (N_{D1} - N_{D2}) \Delta x_1.
\]  

(5)

By a similar analysis,\(^{12} \) we obtain for the diffusion potential due only to the HJ dipole,

\[
V_D(0) = V_{Dk} + q/2k \left[ (\sigma_i (x_1 - d/2) - (N_{D1} - N_{D2}) \Delta x_1/2 \right].
\]  

(6)

In deriving Eq. (6), we assume the interface traps are uniformly distributed in a region of width, \( d \). In other words, \( V_{Dk} \) is the total potential drop due to the superposition of the intrinsic heterojunction electrostatic potential \( V_{D1}(0) \), and the potential due to monopolar interface defects \( \left( \frac{q}{2k} \sigma_i d \right) \). Interface states which are dipolar in nature, however, are indistinguishable from the intrinsic HJ dipole and can potentially induce error in the determination of \( V_D(0) \), provided such defects are present.

Note that \( V_D(0) \) approaches \( V_{Dk} \) as \( d \) or \( \sigma_i \) are decreased. Thus, measurements of \( \Delta E_c \) using the depletion technique along with Eqs. (2) and (3) are only accurate in the absence of interface traps, or for very abrupt HJs. On the other hand, if \( d \) is large and \( V_{Dk} \) is small, the second and third terms on the right in Eq. (6) may become larger than the measured value of \( V_{Dk} \). One example of HJs in which \( V_{Dk} \) differs significantly from \( V_D(0) \) is p-P Hg\(_3\)Cd\(_3\)Te/Cd(4% Zn)Te heterojunctions measured in recent work.\(^{15} \) There it was found that \( d \approx 0.3 \mu \text{m} \) and \( \Delta E_s = 100 \text{ meV} \). In that case, \( V_D(0) \) was found to be five times larger than \( V_{Dk} \).

Also note that monopolar defects (either donors or acceptors) are indistinguishable from shallow dopants. Thus, the net trap charge density calculated via Eq. (2) may arise from the wrong choice of \( N_{D1} \) or \( N_{D2} \). Indeed, one problem with using Eqs. (2) and (3) is the assumption that \( N_{D1} \) and \( N_{D2} \) are known in the interface region, and that these values change abruptly at \( x^*_1 \) (see Fig. 1). However, if any doping nonuniformities occur over the heterointerface width, \( d \), we can use both Eqs. (5) and (6) to eliminate this error source to obtain the exact value of \( V_D(0) \). In many cases the assumption that variations in doping occur over a distance \( d \) is justified since diffusion of dopants, semiconductor constituents, and defects will probably be most pronounced over the same spatial region. Indeed in most experiments reported using Eqs. (2) and (3), a value of \( \sigma_{iK} (1-3) \times 10^9 \text{ cm}^{-2} \) is often observed. While this value may in fact be due to the
presence of interfacial defects or even arise from limited experimental resolution, it can also be explained as simply due to deviations of $N_{D1}$ and $N_{D2}$ from their bulk values in the heterointerface region.

As inferred from Eqs. (5) and (6), $\Delta x_c$ and $d$ are the only two unknowns needed to obtain the exact trap density and diffusion potential using the measured values of $\sigma_{kr}$, $V_{DK}$, $N_{D1}$, and $N_{D2}$. The width of the interface region ($d$) can be measured independently; for example, using secondary ion mass spectroscopy (SIMS) or other microscopically obtained data. Also, $\Delta x_c$ can be found using Fig. 2(a) where it is plotted versus both $\sigma_{kr}$ and $N_{D1}$. These curves, which have been determined via a computer solution to Poisson’s equation for HJs where rectifying contact is made to the semiconductor layer which is depleted at the heterointerface, assume that $\Delta E_c = -0.12$ and $-0.36$ eV. These curves are independent of $N_{D1}$ in the range $1 \times 10^{13} < N_{D2} < 5 \times 10^{16}$ cm$^{-3}$. Here, each curve is obtained by specifying values of $d$ and $\Delta E_c$, although $\Delta x_c$ is found to be relatively insensitive to $d$. For example, as $d$ is varied from 50 to 500 Å, the variation of $\Delta x_c$ is less than 2%. Furthermore, $|\Delta x_c|$ decreases linearly as $\Delta E_c$ increases from 0 to $-0.5$ eV, independent of doping level and interface charge density ($\sigma_{kr}$). Hence, for any value of $\Delta E_c$ within this range, the dependence of $|\Delta x_c|$ on $\sigma_{kr}$ can be found by interpolation from the values shown in this figure. The error incurred by obtaining $\Delta x_c$ for a particular $\sigma_{kr}$ via interpolation is less than 5%. Finally, note that $\Delta x_c$ is relatively insensitive to the effective conduction band density of states $N_c$ of both HJ materials. For example, as $N_c$ increases from $3 \times 10^{11}$ to $3 \times 10^{14}$ cm$^{-3}$, the variation of $\Delta x_c$ is only 4% (where $N_{D1} = N_{D2} = 6 \times 10^{13}$ cm$^{-3}$ and $\sigma_{kr} = 5 \times 10^{10}$ cm$^{-2}$ are assumed).

In Fig. 2(b) we plot $\Delta x_c$ vs $\sigma_{kr}$ for a HJ with the opposite symmetry to that in Fig. 2(a). Thus, in this plot the rectifying contact is made to the material which is accumulated at the heterointerface (e.g., $n$-In$_{0.53}$Ga$_{0.47}$As). In comparison with Fig. 2(a), $\Delta x_c$ is positive, and the absolute value of the shift in $x^*$ is smaller for this HJ type. Hence, the deviation of $V_{DK}$ from $V_{D}(0)$ can be reduced by preparing samples where the rectifying contact is made to the material which has carrier accumulation in the HJ region. Finally, also note that these curves are insensitive to $N_{D2}$, as compared with $N_{D1}$, as shown in Fig. 2(a). This indicates that $\Delta x_c$ is strongly determined by the doping concentration of the material which is depleted near the HJ, where the Debye length is larger.

III. EXPERIMENT

Using Eqs. (5) and (6) in conjunction with Fig. 2(a), $V_{DK}(0)$ and $\sigma_{kr}$ were obtained for a $N-n$ InP/In$_{0.53}$Ga$_{0.47}$As isotype heterojunction grown by hydride vapor phase epitaxy (VPE) on (100) $n^+$-InP substrates S-doped to $5 \times 10^{18}$ cm$^{-3}$. The first layer grown was an approximately 1-μm-thick InP buffer layer, followed by 4 μm of adventitiously doped $n^-$-In$_{0.53}$Ga$_{0.47}$As. Next, a 0.6-μm-layer of S-doped N-InP was grown, and the final layer was a 1.2-μm-thick, undoped N$^+$-InP cap. A rectifying organic-on-inorganic (OI) semiconductor contact was formed on the top N$^+$-InP surface using the organic compound, 3,4,9,10-pyrenyletetra-carboxylic dianhydride via fabrication techniques discussed previously. The free carrier concentration profile for the sample which was obtained by reverse biasing the OI contact is shown by the solid line in Fig. 3.

SIMS data for this sample are shown in the inset of Fig. 3. From the indium and sulfur concentration profiles, the $N^+$-InP, N-InP, and $n^-$-In$_{0.53}$Ga$_{0.47}$As layers can be identified. The heterointerface region width (cross-hatched area)
is inferred from the gradual drop of both the indium and sulfur concentrations at the N-InP/In0.53Ga0.47As interface. The heterointerface width is estimated from these data to be $d = (350 \pm 50)$ Å.

From the free carrier concentration profile of Fig. 3, we obtain $N_{D_1} = (1.00 \pm 0.02) \times 10^{16}$ cm$^{-3}$, $N_{D_2} = (6.00 \pm 0.05) \times 10^{15}$ cm$^{-3}$, and $x^*_f = (1.83 \pm 0.01)$ μm.

Using Eqs. (2) and (3), we calculate $\sigma_k = (1.8 \pm 0.3) \times 10^{10}$ cm$^{-2}$ and $V_{DK} = -(0.21 \pm 0.01)$ V. Taking the electron effective masses$^{18}$ of InP and In0.53Ga0.47As as 0.07$m_0$ and 0.04$m_0$, where $m_0$ is the free-electron mass, we obtain $\Delta E_{ck} = -(0.22 \pm 0.01)$ eV.

Using $\sigma_K$ and $\Delta E_{ck}$, we determine $\sigma_f$ and $\Delta E_f$ as follows: From Fig. 2, $\Delta x_f$ is obtained by linear interpolation using the curve corresponding to $\Delta E_f = \Delta E_{ck}$—the latter value being our first best estimate for the band discontinuity energy. In this manner, we obtain $\Delta x_f = -(250 \pm 12)$ Å. Substituting$^{19}$ $d$, $\Delta x_f$, $\sigma_K$, and $\Delta E_{ck}$ into Eqs. (5) and (6), we get $\Delta E_f = -(0.24 \pm 0.01)$ eV and $\sigma_f = (2.7 \pm 0.4) \times 10^{10}$ cm$^{-2}$. More accuracy in these latter two parameters can be achieved by iteratively repeating the process, always replacing $\sigma_f$ and $\Delta E_f$ in Eqs. (5) and (6) with the new values of $\sigma_f$ and $\Delta E_f$ thus obtained. The iterations are discontinued when the difference between both sides of Eq.(6) becomes negligibly small. In the present example, only a single iteration was required. Note that while $\Delta E_{ck}$ and $\Delta E_f$ differ by only 10% for this sample, $\sigma_f$ is roughly twice $\sigma_K$, consistent with our discussion of Fig. 1 due to the sensitivity of this parameter to the choice of $N_{D_1}$ and $N_{D_2}$.

The ability of Eqs. (5) and (6) to correct for the effects of fixed charge was further tested using a more extreme, albeit artificial example by assuming $N_{D_1} = 7 \times 10^{16}$ cm$^{-3}$ for the sample in Fig. 3 instead of its actual value of $N_{D_1} = 1 \times 10^{16}$ cm$^{-3}$. In this case, we set $d = d'$ equal to the integration limit on the InP side of the HJ, thereby "assigning" the difference between $N'_{D_1}$ and $N_{D_1}$ to fixed interface charge. Following this procedure, we obtained $V_{DK} = -0.06$ V, and after two iterations using Eqs. (5) and (6) and Fig. 2, we obtain, once more, the actual value of $V_{D}(0) = -0.23$ V and $\sigma_f = (N_{D_1} - N_{D_1})/d' + \sigma_f$. This example, although somewhat contrived, indicates the ability of the approach to achieve accurate values for $\Delta E_f$ even in the presence of a very high density of fixed charge.

In order to check the accuracy of $\sigma_f$ and $\Delta E_f$ obtained for the InP/In0.53Ga0.47As HJ, the apparent free carrier concentration profile $[n^*(x^*)]$ near the HJ was calculated assuming $\Delta E_f(0) = -0.24$ eV, $d = 350$ Å, and $\sigma_f = 2.7 \times 10^{10}$ cm$^{-2}$. This calculated $n^*(x^*)$ profile is shown by the dashed line in Fig. 3. The agreement between the experimental and calculated profiles is quite good, except that the peak value at $x^*$ for the experimental data is lower. This also represents an improved fit over that which was obtained using $\sigma_{ck}$ and $\Delta E_{ck}$ inferred from Eqs. (2) and (3). We attribute the difference in peak values at $x^*$ to the interfacial compositional gradient which tends to lower the measured peak due to a spatial broadening of the HJ dipole.

To our knowledge, these are the first measurements of the conduction-band discontinuity energy of hydride VPE grown N-n InP/In0.53Ga0.47As HJs. These data are consistent with data$^{20}$ for molecular-beam epitaxially grown samples for this same heterojunction, and furthermore, they are consistent with data for liquid phase epitaxially grown n-N In0.53Ga0.47As/InP HJs.$^{13}$ This implies that the measured conduction-band discontinuity energy is independent of growth sequence for (100) In0.53Ga0.47As/InP heterojunctions.

IV. SUMMARY AND CONCLUSION

In conclusion, we have described a means for improving the measurement accuracy of the interface trap density and band-edge discontinuity energy obtained from capacitance-voltage analysis, and have used it to study hydride vapor phase epitaxially grown InP/In0.53Ga0.47As HJs. This approach is especially useful for the measurement of band discontinuity energies of samples with high densities of shallow acceptor traps ($\sigma_f < 0$), or with large differences in free carrier concentrations between the contacting materials. The diffusion potential obtained from this improved C-V technique is insensitive to variations in doping and trap density in the interface region.

The technique is simple to use, and can give an a priori estimate of the accuracy of the band offset measurement. For relatively trap-free HJs whose offset magnitude is much greater than $kT$, the values for $\Delta E_f$ obtained using the conventional depletion technique$^{1}$ can be accurate to within 10–20 meV. For smaller offsets, or for HJs which have a non-negligible trap density (e.g., HgCdTe/CdTe), the conventional methods can lead to large inaccuracies. In these cases, the techniques discussed here can give an accurate value for $\Delta E_f$, which is several times larger than the measured values using previous methods. To our knowledge, this improved capacitance-voltage technique is the most accurate means available for determining the interface trap density and band discontinuity energies of semiconductor heterojunctions.
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19Equation (6) can be rewritten in terms of $\Delta E$ and $\Delta E_\text{me}$ simply by replacing $V_0(0)$ and $V_{DE}$, respectively, with these band offset energies.
Determination of free carrier concentration profiles and the valence-band discontinuity energy of Hg_{0.7}Cd_{0.3}Te/Cd(4% Zn)Te heterojunctions using organic semiconductor layers

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Capacitance-voltage data are utilized to obtain the free-carrier concentration in n- and p-type Hg_{1-x}Cd_{x}Te layers, and to measure the valence-band discontinuity energy of a p-type Hg_{0.7}Cd_{0.3}Te/Cd(4% Zn)Te isotype heterojunction. To facilitate measurement, rectifying contact was made to the Hg_{1-x}Cd_{x}Te layers using one of two organic materials—metal-free phthalocyanine and copper phthalocyanine. Contrary to previous results with this heterojunction system, we find that holes are accumulated near the Cd(4% Zn)Te side (rather than Hg_{1-x}Cd_{x}Te side). We obtain a valence band discontinuity energy (\Delta E_v) equal to (110 \pm 20) meV, and a fixed interface charge density of \sigma = -(5.9 \pm 0.3) \times 10^{10} cm^{-2}.

Heterojunctions (HJ) in the Hg_{1-x}Cd_{x}Te (MCT) materials system are assuming increased importance for a number of device applications such as photovoltaic and photoconductive infrared detectors. Since the lattice parameters of HgTe and CdTe are nearly equal, the lattice-matched epitaxial growth of Hg_{1-x}Cd_{x}Te for all values of y may be obtained on CdTe substrates, thus minimizing the density of defects associated with misfit dislocations. Moreover, it is found that lattice matching can be further improved by using Cd_{1-x}Zn_{x}Te with x \approx -0.04 instead of CdTe for the substrate.

Band-edge discontinuities are of central importance in determining device behavior. However, our understanding, both theoretical and experimental, of the valence-band discontinuity in MCT heterojunctions is far from being complete. From the phenomenological common anion rule and Harrison’s linear combination of atomic orbitals (LCAO) calculations without dipole contributions, it is deduced that the valence-band offset at the CdTe-HgTe interface is small (with \Delta E_v < 0.1 eV). Magneto-optical measurements and resonant Raman spectra obtained at low temperature on HgTe-CdTe superlattices also indicate that \Delta E_v is small. On the other hand, a larger valence-band offset of 0.35 eV has been obtained at room temperature by x-ray photoemission spectroscopy (XPS), consistent with values predicted by Tersoff’s interface quantum-dipole model (where \Delta E_v = 0.5 eV), and the LCAO calculation which includes the contribution due to dipoles (\Delta E_v = 0.49 eV). In addition, recent tight binding calculations which include the contribution of the cation d orbitals give a natural valence-band offset of 0.36 eV, which is very close to the XPS results.

The discrepancy between the experimental results obtained by these several techniques has been suggested to be due to the temperature dependence of the valence-band discontinuity. For example, temperature-dependent data of the valence-band discontinuity obtained from direct electrical measurement have been reported. However, the existence of parasitic transport mechanisms which were not considered in that work may lead to erroneous values of \Delta E_v.

In our work, capacitance-voltage analysis combined with the use of organic thin-film contacts is used to obtain free-carrier concentrations deep into the bulk of the sample. In addition, the depletion method proposed by Kroemer et al. is utilized to measure the band offset of MCT HJs. This technique is relatively insensitive to compositional gradients at the heterojunction, and therefore it is particularly useful for studying Hg_{1-x}Cd_{x}Te/CdTe heterojunctions which can have a significant grading length due to the interdiffusion of Hg and Cd atoms at the heterointerface. Another property of this technique is that the band bending near the HJ can be inferred from the carrier concentration profile simply by observing the location of the carrier accumulation and depletion regions. This is different from optical techniques which only measure the relative energy levels of the valence- (or conduction-) band edges of the two contacting materials.

The C-V measurements are accomplished by depleting the semiconductor in the region of the heterojunction by applying reverse bias voltage across an adjacent rectifying contact. The apparent free-hole concentration \( p^*(x^*) \) at the edge of the depletion region a distance \( x^* \) away from the contact is obtained using

\[
p^*(x^*) = \frac{2}{q}\frac{dV}{d(1/C_D)} \text{,}
\]

with \( x^* = \kappa A / C_D \), where \( A \) is the junction area, \( C_D \) is the diode capacitance, \( \kappa \) is the permittivity of the semiconductor, \( V \) is the reverse bias voltage, and \( q \) is the electronic charge. The background carrier concentration \( N_s \) on both sides of the p-P HJ can be determined by measuring \( p^*(x^*) \) at distances far removed from the heterointerface. The apparent position of the HJ \( x^* \) is obtained from the location of the peak in \( p^*(x^*) \) corresponding to charge accumulation in at the HJ. Using these data, the density of fixed charge in the heterointerface region and the built-in potential \( V_{bK} \) of the HJ dipole can be calculated using

\[
\sigma = \int (N_s(x) - p^*(x^*)) dx^* \text{,}
\]

where \( N_s(x) \) is the background carrier concentration, and \( p^*(x^*) \) is the apparent free-hole concentration at the heterointerface.
It has been shown that \( V_{DK} \) can differ significantly from that due solely to the HJ dipole potential, \( V_D \), in the presence of a sufficiently high density of interface charge. In addition, due to inherent limitations of the spatial resolution of \( C-V \) data, the actual HJ position \( (x) \) is shifted from \( x^* \) by \( \Delta x = x - x^* \), which depends on the magnitude of \( \sigma \) and \( V_{DK} \). When these factors are considered, the HJ dipole potential can be obtained using

\[
V_D = V_{DK} + q\sigma(d/2 + \Delta x)/\kappa,
\]

where \( d \) is the thickness of the heterointerface region. The relationship between the valence-band discontinuity energy and \( V_D \) can finally be calculated using \( \Delta E = \delta_2 - \delta_1 - \left| qV_D \right| \), where \( \delta_1 \) and \( \delta_2 \) are the depths of the Fermi levels as measured from the valence-band maxima in the Hg$_{1-\gamma}$Cd$_\gamma$Te and Cd(4\% Zn)Te bulks, respectively.

One impediment to the measurement of free-carrier concentrations is the difficulty in forming a rectifying contact to MCT. Schottky barrier diodes are subject to low voltage breakdown, hence giving rise to large reverse leakage currents which degrade the accuracy of the capacitance measurement. Therefore, we use organic-on-inorganic (OI) contact barrier diodes to form rectifying contacts to the Hg$_{1-\gamma}$Cd$_\gamma$Te. Due to the anisotropy of the conductivity of the organic film, current is confined to the region under the organic film, with areas of \( \sim 10^{-4} \) cm$^2$. To contact the MCT, an In$_{0.4}$Zn$_{0.6}$Te bulks, respectively, at different temperatures (down to 100 K). The breakdown voltage of 8 V at \( T = 100 \) K (defined at reverse dark current of 10 \( \mu \)A) is considerably larger than the \( < 1 \) V breakdown observed for metal/MCT Schottky barrier diodes. Majority carrier types are deduced from the polarity of the \( I-V \) characteristics, and are consistent with the doping of the MCT layers during growth.

From these data we deduce a Hg$_{1-\gamma}$Cd$_\gamma$Te barrier energy of \( \phi_B = 0.41 \pm 0.04 \) V.

Carrier concentration profiles taken from diodes along the taper were obtained from \( C-V \) data measured at 1 MHz at different temperatures (down to 91 K). No appreciable temperature dependence of the carrier concentration is observed. From the room-temperature profiles, the composite carrier concentration profile from the top \( n \) layer through the \( p \) layer to the Cd(4\% Zn)Te substrate is obtained as shown in Fig. 2. The location of the peak in the concentration profile indicates that the Hg$_{1-\gamma}$Cd$_\gamma$Te/Cd(4\% Zn)Te/HJ layer is at 8.5 \( \mu \)m, consistent with microscopic measurement. Further, we obtain a free-carrier concentration of \((1-2) \times 10^{16} \) cm$^{-3}$, \( 4 \times 10^{16} \) cm$^{-3}$, and \( 5 \times 10^{14} \) cm$^{-3}$ for the \( n-Hg_{1-\gamma}Cd_{\gamma}Te, p-Hg_{1-\gamma}Cd_{\gamma}Te, \) and \( p-Cd(4\% Zn)Te \) layers, respectively.

The free-carrier concentration profile shown in Fig. 3 was measured at 91 K using a device located 6.6 \( \mu \)m from the original surface. We observe that holes are accumulated at the Cd(4\% Zn)Te side giving rise to a peak in \( n^+(x^*) \), and depleted from the Hg$_{1-\gamma}$Cd$_\gamma$Te side of the HJ. This implies that the band bending of both materials near the HJ is as

\[
V_{DK} = \frac{q}{\kappa} \int \left[ N_d(x^*) - p^*(x^*) \right] (x^* - x^*) \, dx^*.
\]

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**FIG. 1.** Bipolar current-voltage characteristics of an In$_{0.4}$Zn$_{0.6}$Te diode at two different temperatures. Open circles: 296 K, solid circles: 100 K. Inset: Typical bipolar current-voltage characteristics of an In$_{0.4}$Zn$_{0.6}$Te diode (solid line) and In$\text{Cd}(4\% Zn)Te$ diode (dashed line). The two are plotted using opposite bias polarity for comparison. Scales are vert: 10 \( \mu \)A/div, hoz: 2 V/div.
shown in the inset, i.e., the valence band of Cd(4% Zn)Te lies above that of Hg0.7Cd0.3Te at the HJ. This is contrary to previous work indicating that the valence band of CdTe is lower in energy than that of HgTe.13,14,15

From the profile shown in Fig. 3, a valence-band potential energy of $qV_{OX} = (25 \pm 4)$ meV is obtained via Eqs. (2) and (3). The density of fixed charge is calculated via Eq. (2), giving $\sigma = -(5.9 \pm 0.3) \times 10^{10}$ cm$^{-2}$, the negative sign indicating that the interface traps are acceptor-like. Using these values of $\sigma$ and $V_{OX}$ in Eq. (5), we obtain a valence-band offset13,20 of $\Delta E_v = (110 \pm 20)$ meV.

To check the accuracy of the measured $\Delta E_v$, the carrier concentration profile was "reconstructed" by solving Poisson’s equation using the valence-band energy $\Delta E_v$ and interface charge density given above. To accomplish this fit, we assume a width20 for the interface region of $d = 3000 \text{ Å}$. We note, however, that the quality of the fit is not strongly dependent on the value of $d$ chosen. As shown in Fig. 3, the agreement between the measured hole concentration profile and the simulation result is quite good, providing an independent check of our values for $\Delta E_v$ and $\sigma$.

In conclusion, HgPc and CuPc are found to form rectifying contacts to HgCdTe. This allows the use of the C-V depletion technique to measure the free-carrier concentrations and the valence-band discontinuity energy of HgCdTe/Cd(4% Zn)Te heterojunction samples. A valence-band discontinuity, $\Delta E_v$, equal to $(110 \pm 20)$ meV is obtained at 91 K, with the hole accumulation region at the Cd(4% Zn)Te side, rather than the Hg0.7Cd0.3Te side of the heterointerface. Because the direction of the offset is different from that reported in the literature, several alternative explanations have been considered. If impurity buildup at defects in the junction region had caused an n-type region to be present in the HgCdTe, this would introduce a $p$-$n$ junction above the heterojunction. If this were the cause of the structure in $p^*(x^*)$, the apparent carrier concentration would be expected to increase at the $p$-$n$ junction to a very large value, and the profile on the far side would not be observed. Alternatively, the acceptor concentration might vary in the narrow HJ region in such a way as to "mimic" a typical HJ profile as shown in Fig. 3. However, this is considered unlikely because of the complicated "dipolar" form of the impurity concentration which would be required to produce such a peak. While these interpretations cannot be ruled out completely, the data presented for the HgCdTe/Cd(3%)Te heterojunction are of a quality comparable to the best data taken on the GaAs/AlGaAs11 and InGaAsP/InP14 systems that did give verifiable offsets.

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20For this calculation, we take $d = 3000 \text{ Å}$ which is typical of our samples.
Growth and characteristics of organic-on-inorganic semiconductor heterostructures

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Growth and Characteristics of Organic-on-Inorganic Semiconductor Heterostructures

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ABSTRACT

Recently, several crystalline organic semiconductors have been found to form rectifying heterojunctions when deposited onto inorganic semiconductor substrates. In this paper, we discuss the growth and characterization of these organic-on-inorganic (OI) heterostructures. Both the purification of organic materials, and the fabrication procedures for OI heterostructures are described in detail. The electrical properties, as well as the microstructure of the organic material are found to be very sensitive to the deposition conditions. The valence band discontinuity at the OI heterojunction is measured for the first time, using both forward current-voltage characteristics and internal photoemission. The interface state densities have been studied for several different organic semiconductors deposited on p-Si substrates. A model is proposed to account for the observed results.

I. Introduction

In the past ten years, considerable effort has been focused on the study of semiconductor heterojunctions. Understanding the nature of these heterojunctions (HJ's) is essential if we are to use them to advantage in many semiconductor devices such as lasers and photodetectors. More recently, there have been a few reports on an entirely new class of semiconductor heterostructures which are also potentially useful for optoelectronic device applications. These HJ's consist of an organic (crystalline molecular or polymeric) semiconductor in contact with an inorganic semiconductor, which form rectifying energy barriers at the organic-on-inorganic (OI) semiconductor interface. The resulting rectifying characteristics of the OI-HJ's have been attributed to the low reactivity between the deposited organic materials and the inorganic substrate, and to the low energy associated with the deposition of the thin films. These factors enable one to use OI heterostructures in non-destructive surface analysis of inorganic semiconductors.

In this paper, we discuss the different aspects of the growth of OI heterostructures, including the purification of organic materials and the techniques for device fabrication. The nature of the OI heterointerface and band discontinuities also be discussed in detail.

II. Growth of OI-HJ Heterostructures

Purification Organic Material

The organic materials that have been used most extensively in OI-HJ’s are aromatic compounds, such as 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA). These materials are crystalline molecular solids which are both thermally and hydrolytically stable. We present here the purification procedures for PTCDA; and it is noted that the procedures for purifying other organic materials are similar. It is critical that all organic materials be purified prior to deposition onto inorganic substrates. This ensures highly stable and reproducible electrical and optical characteristics of the resulting devices.

PTCDA is available commercially in powder form. Among the different methods to purify PTCDA, gradient sublimation gives the highest purity source material. To purify PTCDA, a few grams of powder are put into the sealed end of a quartz tube. The tube is evacuated to about 10^{-5} torr, and the closed end of the tube is inserted into a preheated furnace. The sample is kept at 425-450°C (i.e. just below the sublimation temperature of PTCDA) during the process of purification, which proceeds for between 24 and 48 hours. After this period, the tube is cooled while the sample is maintained under vacuum. The wall of the tube shows bands of different colors. Only the dark red, unsublimed source material is used for fabrication of OI heterostructures.

Crystal and Molecular Structure of the Organic Thin Films

In order to understand the electrical properties of the OI heterojunction, it is necessary to study the crystal structure of these organic materials. For example, PTCDA is a monoclinic crystal, that forms infinite stacks of planar, uniformly spaced molecules in which the atoms of one molecule are located directly above adjacent molecules, as shown in Fig. 1. The interplanar spacings for several crystalline organic solids used in OI HJ's are shown in Table I. The most important aspect of the crystal structure of PTCDA is its extremely small interplanar spacing of 3.21 Å, which is even smaller than that of graphite (3.37 Å). Thus, the π-orbitals overlap to the extent that car-
Carriers moving along the stacking axis are highly delocalized, giving rise to a significant anisotropy of electrical conductivity when measured with respect to the crystalline axes. Typical anisotropies range from 10-1000.

Anisotropy can also be caused by the presence of grain boundaries in the organic films. The deposited organic films are polycrystalline, with a grain size on the order of several thousand angstroms. Carriers moving in the vertical direction are not likely to cross the grain boundaries if the organic film is thin enough (<2000 Å). On the other hand, carriers moving along any in-plane directions will be trapped at the grain boundaries and therefore the mobility is drastically reduced, resulting in additional anisotropy in conductivity.

### III. Fabrication of Organic Heterostructures

Many molecular semiconductors such as PTCDA, NTCDA, CuPc, and the phthalocyanines (Pc's) have been used to form QI-HE's with a variety of inorganic semiconductor substrates. Here we give a brief outline of the fabrication procedures with additional detail given in the literature. The first step in the fabrication of the QI heterostructure is wafer cleaning. Organic solvents are used for degreasing, which is followed by native oxide etching in a dilute HF solution. For some III-V compounds such as InP and related materials, enhancement of the contact barrier can be achieved by oxidizing the samples in a solution such as HNO₃ and H₂O₂. Table II gives the cleaning sequence used to prepare several common inorganic semiconductors. The final step in surface preparation is a rinse in deionized water, followed by drying of the wafer with filtered nitrogen gas.

![Fig. 1: Perspective view of the unit cell of PTCDA looking from (a) a-axis and (b) b-axis.](image)

<table>
<thead>
<tr>
<th>Table II Cleaning Sequence For Some Semiconductors&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>Si</td>
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<tr>
<td>GaAs</td>
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<tr>
<td>InP</td>
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<sup>a</sup>Surface treatments all follow a thorough organic solvent cleaning. Wafers should be rinsed in D.I. water for 5 min. after etching with acid.

Immediately after cleaning, the sample is loaded into a vacuum chamber which is pumped down to <10⁻⁶ torr. Next, 1000-2000 Å of the organic material is vacuum sublimed onto the pre-cleaned top surface of the wafer. Organic materials generally have low sublimation temperature in the range between 100°C and 600°C. Good control of the deposition parameters can be achieved by using a two-chamber source boat such as that employed for silicon monoxide deposition. Typical deposition rates for organic materials are 30-40 Å/s. Next, ohmic contact metal pads 2000-3000 Å thick are evaporated onto the organic film. The contact metals used for some organics are also listed in Table I. Finally, a full surface ohmic contact metal is evaporated onto the back side of the wafer.

### Table I

| Interplanar spacing and ohmic contact metals used for some organic semiconductors |
| PTCDA | NTCDA | CuPc | H₂Pc |
|-------------------------------|
| Interplanar Spacing (Å) | 3.21 | 3.51 | 3.38 | 3.40 |
| Contact metal | In, Ti | In | Au | In |

It has been found that the microstructure and surface morphology of some aromatic compounds are very sensitive to both deposition rate and substrate temperature. For instance, thin films of PTCDA deposited at high deposition rates (50-100 Å/s) show strong preferred orientation. The crystalline perfection of films deposited at a high rate is demonstrated by the x-ray pole figure for the (102) interplanar diffraction peak as shown in Fig. 2(a). In sharp contrast, no preferred orientation is observed for films deposited slowly (2 Å/s), as shown in Fig. 2(b). It is noted that Kim et al. have observed that the surface morphology is better for organic films deposited at low substrate temperatures than those deposited at high temperatures. Therefore, substrate temperature also plays an important role in determining the microstructure of the organic film.

The effect that the microstructure of PTCDA has on electrical properties is apparent from Fig. 3. For films deposited at 100 Å/s, the carrier mobility can be as high as 1.4 cm²/V-s, which is an order of magnitude larger than that for the films deposited at lower deposition rates. These results can be explained in view of the crystalline order of the films. A higher order implies fewer grain boundaries, and hence a reduced charge trapping at these imperfections. The existence of traps in the more disordered film is consistent with the hysteresis often observed in the current-voltage characteristics.

IV. Measurement of Valence Band Discontinuity Energies

Knowledge of the band discontinuity energies is essential to the understanding of any semiconductor heterojunction. For the first time, we have measured the energy band discontinuity of an OI-HJ. In this experiment, the sample was an isotype (p-P) PTCDA/p-Si heterojunction investigated using the temperature dependence of the I-V characteristics as well as internal photoemission spectroscopy.

It can be shown that the forward I-V characteristics are described by

\[
J = J_0 \exp(-qV_D/kT)[\exp(qV_D/kT) - 1] = J_s[\exp(qV_D/kT) - 1] \quad (1)
\]

Here, \( k \) is the Boltzmann’s constant, \( T \) is the temperature, \( q \) is the electronic charge, \( J_s \) is the saturation current and \( V_D \) is the OI-HJ barrier potential. Also, \( V_D \) is the voltage drop across the depletion layer of the inorganic semiconductor which is taken to be positive under forward bias.

From Eq.(1), it is apparent that a measurement of the saturation current as a function of temperature will give its activation energy. A plot of \( \log(J_s) \) as a function of \( 1/T \) is shown in Fig. 4. A schematic cross-sectional drawing of an organic-on-inorganic semiconductor heterojunction device is shown in the inset.

Fig. 3: Carrier mobility in PTCDA as a function of deposition rate.

![Fig. 2: X-ray pole figure of the (102) reflection intensity of PTCDA deposited at (a) >50A/s and (b) approximately 2Å/s. Each contour represents a 10% and 2% change in peak intensity for (a) and (b) respectively.](image-url)
least square fit to the data, as indicated by the straight line, gives $E_p = 0.36 \pm 0.02$ eV. The valence band discontinuity, $\Delta E_v$, for this isotype heterojunction is obtained from $E_p$ using $^{19}$

$$\Delta E_v = q \mp E_p + \delta_s - \delta_o$$

where $\delta_s$ and $\delta_o$ are the differences between the Fermi-level and the valence band maximum in the inorganic and organic bulk semiconductors. Taking the p-Si hole concentration to be $5 \times 10^{15}$ cm$^{-3}$, a hole concentration$^9$ of $5 \times 10^{14}$ cm$^{-3}$ for PTCDA, and assuming the effective hole mass ($m^*$) in PTCDA is equal to the free electron mass, we obtain $\Delta E_v = (0.48 \pm 0.2)$ eV for a PTCDA/p-Si heterojunction. Note that the band gap of PTCDA is $2.2$ eV. Therefore, $\Delta E_v = \Delta E_g - \Delta E_v = 0.6$ eV where $\Delta E_g$ is the difference in band gap energies between PTCDA and Si.

We have also measured $\Delta E_v$ directly by internal photoemission spectroscopy. In this experiment, a PTCDA/p-Si heterostructure was illuminated through the Si substrate using a chopped light source, such that light with energy greater than $1.1$ eV is filtered by the substrate. Further attenuation of short wavelength light was achieved by inserting a second Si wafer between the sample and the light source. The short circuit photocurrent was then measured as a function of photon energy. Fig. 5(a) shows a photoemission spectrum where a peak is found at $h\nu = 0.57$ eV. The results can be interpreted as follows: At $h\nu < 0.57$ eV, holes in the organic film are photo-excited, and subsequently emitted over the $E_i$ energy barrier. This photoemission current is expected to follow: $I_{ph} = (h\nu - \Delta E_v)^2$. Fig. 5(b) shows a plot of the square root of photocurrent versus $h\nu$ for the data taken on the long wavelength side of the emission peak. A least squares fit to these data gives $\Delta E_v = (0.50 \pm 0.1)$ eV -- a value which agrees with that obtained from the forward I-V characteristics.

Note that at $h\nu > 0.57$ eV, $I_{ph}$ drops rapidly to zero. This can be understood using the band diagram shown in the inset of Fig. 5(a). Molecular semiconductors are characterized by narrow bandwidths, as indicated by the cross-hatched region in the figure. For PTCDA, the total bandwith (BW), which is the sum of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bandwidths, is only $0.9$ eV. Thus, transition "b" beyond the BW is forbidden, resulting in a drop in $I_{ph}$ for high energy photons.

![Fig. 5a: Photocurrent spectrum for an In/PTCDA/p-Si heterojunction illuminated via the p-Si substrate. The organic film thickness is 1000 Å. Inset: Band diagram of a PTCDA/p-Si heterojunction showing allowed ("a" and "c") and forbidden ("b") photoemission transitions resulting in the spectrum shown.](image)

![Fig. 5b: Square root of the photocurrent versus photon energy for the data on the long wavelength side of the peak shown in 5a. The solid line is a linear least squares fit to the data points.](image)

Fig. 4: Saturation current density ($J_s$) versus $1/T$ for an In/PTCDA/p-Si heterojunction. The solid line is a linear least squares fit to the data points. Inset: Schematic view of an organic/inorganic semiconductor heterojunction device.
Dianhydride containing compounds (such as PTCDA), have been used for semiconductor surface analysis due to their inert nature when deposited onto inorganic semiconductor surfaces. In efforts to study the interactions between the substrate and the organic layer, we have investigated OI-HJs formed using NTCDA, PTCDA and phthalocyanines (H₂Pc and CuPc) deposited on p-Si substrates. The interface state density as a function of surface potential was derived from the MHz capacitance-voltage characteristics. Figure 6 shows was derived from the

The Gibbs free energy (ΔG°) for this reaction is large and negative, implying the reaction is energetically favorable. The CuO molecules formed then diffuse through the surface native oxide layer and participate in the following reaction:

\[ \text{H}_2\text{O} + \text{CuPc} \rightarrow \text{H}_2\text{Pc} + \text{CuO} \]  (3)

The Gibbs free energy (ΔG°) for this reaction is large and negative, indicating the reaction is probable. It should be noted that the interface state density of the CuPc/p-Si heterostructure is peaked at 0.5 eV above the valence band maximum, which corresponds to one of the CuPc acceptor levels of Si. This peak is likely to be due to the presence of free copper, or CuO-Si complexes at the Si surface. A similar reaction might occur at the H₂Pc/p-Si interface where H₂ molecules leave the organic molecules and form H-O-Si complexes, resulting in a high Dss at about the mid-gap of Si. The existence of the high Dss has the effect of pinning the surface Fermi level at the peak in charge density near $V_b = 0.5$ eV.

V. Conclusions

We have described the growth procedures for OI heterostructures. The microstructure and electrical properties of the organic films are very sensitive to the deposition conditions used. We have measured, for the first time, the valence band discontinuity energy for the PTCDA/p-Si heterojunction. This was accomplished using the forward I-V characteristics and internal photoemission spectroscopy data. Finally, we have analyzed the interface state densities of some organic-on-Si devices. In contrast to observations concerning dianhydride-based compounds which are relatively inert, CuPc has been found to react strongly with silicon, resulting in the presence of a high density of interface states which pin the Fermi level at the inorganic substrate surface.

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References


APPENDIX 2
The Effects of Lattice Mismatch on In$_{0.53}$Ga$_{0.47}$As/InP Heterojunctions

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Abstract

The conduction band discontinuities and interface charge densities of several n-N isotype In$_x$Ga$_{1-x}$As/InP ($x = 0.53$) heterojunctions with lattice mismatches ($\Delta a/a$) ranging from +0.26% to -0.24% were measured using capacitance-voltage (C-V) techniques. To facilitate these measurements, organic-on-inorganic contact barrier diodes were used. Extremely low interface charge densities ($< 1 \times 10^{10}$ cm$^{-2}$) are obtained for all the samples, which are approximately one order of magnitude lower than previously reported values for these heterojunctions. We find that the interface charge density is independent of the magnitude of lattice mismatch and temperature. All the samples show a clear peak-and-notch in their apparent free carrier concentration profiles at temperatures as low as 83K. This is in contrast to results reported previously where the notch is observed to disappear at low temperature. The measured heterojunction conduction band discontinuity is also found to be temperature independent, with a value of (0.22 ± 0.02) eV.
The Effects of Lattice Mismatch On In$_{0.53}$Ga$_{0.47}$As/InP Heterojunctions

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It is well known that defects at heterojunctions can affect the performance of optoelectronic devices. For example, lattice-mismatch induced dark-line defects at AlGaAs/GaAs heterojunctions are known to be a principle source of laser degradation [1]. In heterojunction (HJ) systems such as InGaAs(P)/InP where there is no "natural" lattice match condition, great care must be taken during growth to ensure that the composition of the quaternary semiconductor gives a near perfect lattice match. If such a condition is not met, a large number of defects can be generated which propagate from the heterointerface. Other researchers [2,3] have speculated that this lattice mismatch in InGaAs(P)/InP HJs results in a very high density of localized defect charge. The presence of the charge is inferred from a severe distortion in the free carrier concentration profiles of these HJs obtained at low temperature [2,3] using capacitance-voltage (C-V) techniques [4]. To date, however, there has been no systematic study which indicates that this fixed charge, which has
been universally observed in In$_{0.53}$Ga$_{0.47}$As/InP HJs, is in fact due to lattice mismatch.

In this study, we have grown a series of In$_x$Ga$_{1-x}$As/InP heterojunctions in which the lattice mismatch was varied over a very broad range; i.e. from -0.24% to +0.26%. Here, positive mismatch corresponds to compositions of In$_x$Ga$_{1-x}$As whose lattice constant is larger than that of InP. Using C-V techniques, we find that there is no correlation between lattice mismatch and fixed interface charge density. Furthermore, the charge densities measured in our samples are significantly lower than 10$^{10}$ cm$^{-2}$, which to our knowledge represent the lowest values yet reported for In$_{0.53}$Ga$_{0.47}$As/InP HJs. We observe, for the first time, that the free carrier concentration profile measured in the heterointerface region is temperature independent, indicative of the high quality of the HJs studied. From these results, we conclude that the source of the widely observed temperature dependence of these profiles is a result of native defects or impurities introduced during growth, which are noticably absent in our growth process.

As noted above, a good measure of the heterointerface quality is the density of the fixed charges which reside at the heterointerface. The dangling bonds and defects caused by the lattice mismatch, if they are electrically active, should trap free carriers and create fixed interface charges. Kroemer, et al. [4] have shown that the conduction band discontinuity and interface charge density can be determined from the apparent free carrier concentration profiles
obtained from C-V measurements. The band diagram of an n-N isotype Type 1 heterojunction, such as In$_{0.53}$Ga$_{0.47}$As/InP, is shown in the inset of Fig. 1. From this diagram, it is apparent that the conduction band offset energy is related to the diffusion potential $V_D$ across the heterojunction via:

$$\Delta E_C = qV_D + \delta_1 - \delta_2. \quad (1)$$

Here, $q$ is the electronic charge, and $\delta_1$ and $\delta_2$ are the depths of the Fermi levels as measured from the conduction band edges in the large and small band gap layers, respectively. The diffusion potential across the heterojunction, $V_D$, is given by [4]:

$$V_D = q/\epsilon \int_{-\infty}^{\infty} [N_d(x^*) - n^*(x^*)](x^* - x_j)dx^*. \quad (2)$$

The fixed charge density at the heterojunction, $\sigma$, is determined using:

$$\sigma = \int_{0}^{\infty} [N_d(x^*) - n^*(x^*)] \, dx^*, \quad (3)$$

where $\epsilon$ is the semiconductor permittivity, and $n^*(x^*)$ is the measured apparent free carrier concentration determined using standard C-V analysis methods [5]. Also, $N_d(x^*)$ is the background doping concentration which is equal to $n^*(x^*)$ in the InP and In$_{0.53}$Ga$_{0.47}$As layers far away from the heterojunction, and $x_j$ is the actual distance of the heterojunction from the rectifying contact.

Three liquid phase epitaxially (LPE) grown samples have been studied in this experiment. Double crystal x-ray diffraction was used to determine the lattice mismatch between the In$_x$Ga$_{1-x}$As layer ($x =$
0.53) and the underlying InP layer. The lattice mismatches of these three samples are -0.24%, -0.03%, and +0.26%, corresponding to sample #1, #2, and #3, respectively. The variation of lattice mismatch across a (15 mm)$^2$ wafer was found to be less than ±0.03%, for the worst case sample.

The InP and In$_x$Ga$_{1-x}$As layers were grown on (100) S-doped n$^+$ InP substrates with an electron concentration of approximately $3 \times 10^{18}$ cm$^{-3}$. Prior to growth, the substrates were organic solvent cleaned, etched in a solution of 3:1:1 H$_2$SO$_4$:H$_2$O$_2$:H$_2$O for four minutes, and finally rinsed in deionized water immediately before loading into a graphite boat. For surface preservation during heat-up and melt homogenization, the substrate was kept under a Sn-InP melt [6] using a basket inserted into the graphite boat. The growth melt for the In$_x$Ga$_{1-x}$As layer was prepared using ultra-high purity (99.99999+%)[7] In prebaked for 24 hours at 700°C. After the bake, 99.9999% pure polycrystalline InAs and GaAs were added to the melt. Lattice mismatch was achieved by varying the percentage of Ga in the melt. We grew seven wafers with different lattice mismatches, and found that the lattice mismatch was almost linearly related to the atomic percentage of Ga in the melt. For a melt liquidus temperature of 650°C, as X$_{Ga}^l$ is changed from 2.51% to 2.30%, the lattice mismatch ($\Delta a/a$) varied from -0.24% to +0.26%. Here, X$_{Ga}^l$ is defined as the atomic percentage of Ga in the melt. The growth solutions were baked prior to growth for 48 hours at a temperature 20°C higher than the liquidus temperature to reduce the background doping concentrations.
of the layers. The In-InP melt was prepared using prebaked, 99.99999+% In. The melt was then baked for an additional 48 hours after adding a small amount of InP for saturation purposes. The substrate was slid through an undersaturated In-InP melt just before growth to obtain a fresh surface.

A 2-3 μm thick InP buffer layer was grown by the two-phase method [8] at a rate of 0.3 μm/°C, followed by an In_xGa_1-xAs layer grown with 3°C of supercooling at 647°C. The growth rate of the In_xGa_1-xAs layer is strongly depending on the sign and magnitude of the lattice mismatch, varying from 0.6 μm/°C for Δa/a = +0.26%, to 2.1 μm/°C for Δa/a = -0.24%. This result is expected since the growth rate is limited by the diffusion of Ga within the melt. To obtain a uniform layer thickness and smooth surface morphology, the furnace was calibrated to obtain a uniform temperature profile to within ± 0.1°C over a 25 cm length. We found that the surface morphology of negatively lattice mismatched In_xGa_1-xAs layers are generally better than those of positively lattice mismatched ones. In addition, the growth melt can not be wiped off from the wafer surface for In_xGa_1-xAs layers with |Δa/a| > 0.3%.

To facilitate the C-V measurement, organic-on-inorganic (OI) semiconductor contact-barrier diodes were fabricated to form a rectifying contact with the top semiconductor layer [9,10]. These diodes were made in the following manner: A 100Å Cr followed by a 2000Å Au layer were vacuum-deposited to form the contact on the substrate surface. Next, a 1000Å thick layer of the pre-purified
organic semiconductor was vacuum-sublimed onto the epitaxial layer surface of the wafer. The organic compound employed was 3, 4, 9, 10 perylenetetracarboxylic dianhydride (PTCDA). Finally, 5.3 x 10^{-4} \text{ cm}^2 circular In contacts were deposited onto the PTCDA surface through a shadow mask. The organic layer forms a rectifying HJ barrier with the underlying semiconductor such that large reverse bias voltages can be applied to the diode (typically 18V for In_{x}Ga_{1-x}As with a doping of 1 x 10^{15} \text{ cm}^{-3}) without inducing large reverse leakage currents. Usually, the reverse saturation current is less than 10 mA/cm^2, and the sample under study can be deeply depleted prior to undergoing breakdown. A detailed description of the technique of using organic films for wafer analysis is presented elsewhere [9,10].

Capacitance-voltage measurements were performed at temperatures ranging from 293K to 83K. The measurement frequency used was 1 MHz, and the ac test signal amplitude was 10 mV_{rms}. The apparent free carrier concentration profiles of samples #1, #2 and #3 measured at 83K are shown in Fig. 1. As shown in this figure, the peak and notch are clearly evident for all three samples, and no distortion of these profiles from room to low temperature are observed. This result contradicts that of Lang, et al. [11] who suggested that HJ series resistance causes the notch in the In_{0.53}Ga_{0.47}As/InP HJs to vanish at low temperature. By that assumption, this distortion should be observed in all low temperature C-V measurements made on this HJ system, in clear contradiction to our results.
The low and flat free carrier concentrations on both sides of the HJ observed in the profiles in Fig. 1 provide an accurate determination of the background doping concentration \( N_d \). This minimizes the error in calculating the diffusion potential, \( V_D \), and conduction band offset energy, \( \Delta E_C \), using Eq's. (1) and (2). Figure 2 shows the measured conduction band offset energies of these three samples as a function of temperature. As expected, the measured conduction band offset is independent of temperature, and has an average value of \((0.22 \pm 0.02)\) eV. The error bars in the figure are due to the uncertainties in choosing the background doping \( N_d \) on the \( \text{In}_x\text{Ga}_{1-x}\text{As} \) side of the heterojunction. This measured band offset value is consistent with previous reports of \( \Delta E_C \) for \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP} \) HJs measured at room temperature [2,3,11-13]. However, to our knowledge, this is the first time that such a value is found to be completely temperature independent, even though in some cases the lattice mismatch is quite large.

The fixed charge density at the heterointerface is shown in Fig. 3 as a function of temperature. The error bars here are also due to uncertainties in determining \( N_d \). Although there is a small variation in \( \sigma \) at different temperatures, the value of \( \sigma \) is at least one order of magnitude smaller than the values reported previously for \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP} \) HJs [2,3,12,13]. Since the value of \( \sigma \) is so small, the variation in \( \sigma \) with temperature can be attributed to the limitation on capacitance measurement accuracy. The small \( \sigma \) values in our samples also confirm that the filling in of the notch region
in previously reported data [2,3,12,13] is due to charge trapping at a high density of defects at the heterointerface at low temperature. It is surprising that sample #2, which is lattice-matched at the growth temperature, has the highest value of \( \sigma \), whereas sample #3, which has \( \Delta a/a = +0.26\% \), has the smallest \( \sigma \). Thus, we can conclude that lattice mismatch has no effect on creating the heterointerface fixed charge. That is, the defects induced by lattice mismatch are not electrically active. The energy states created by defects at the heterointerface are either pulled into the conduction or valence band at the heterointerface, instead of residing in the band gap region.

In conclusion, we have measured the interface fixed charge density and conduction band discontinuity of three In\(_x\)Ga\(_{1-x}\)As/InP HJs with lattice mismatches ranging from -0.24\% to +0.26\%. The measurements show that the interface charge density is independent of both the magnitude and the sign of the lattice mismatch, contrary to assertions made in previous work. We conclude that the fixed interface charges, therefore, must come from the other sources, e.g. from phosphorus vacancies created during wafer translation [12], or impurities incorporated during growth. In fact, we attribute the very low interface charge densities obtained in this work to the use of ultra high purity In in the growth melt. Experiments in our laboratory with slightly less pure In sources (99.99995\%) show higher values of \( \sigma \) than those reported here, and a detailed report of those experiments will appear elsewhere. The results described here,
therefore, suggest that perfect lattice match is not a strict requirement for devices utilizing this heterojunction system.

From the device processing point of view, slightly negative lattice mismatched LPE-grown In$_{0.53}$Ga$_{0.47}$As might be more suitable for device processing since the surface is smoother than those with perfect or positively mismatched layers. However, for devices requiring thin epitaxial layers, positive lattice mismatch is desired because the growth rate is much slower, and thus the layer thickness is easier to control.

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References


7. Super high mobility grade high purity In (99.99999+%), Nimic Inc., Cupertino, California.


Figure Captions

Fig. 1. Apparent free carrier concentration profiles for sample #1, #2, and #3 measured at 83K. The inset shows the energy band diagram of a typical n-N Type I Heterojunction.

Fig. 2. Measured conduction band offset as a function of temperature for samples #1, #2 and #3.

Fig. 3. Interface fixed charge density as a function of temperature for the three samples in Fig. 2.
Apparent Free Carrier Concentration $n^*(X^*)$ (cm$^{-3}$)

Sample #1

Sample #2

Sample #3

Apparent Position $X^*$ (μm)

$10^{16}$

$10^{15}$

$0.0$ $0.6$ $1.2$ $1.8$ $2.4$ $3.0$