Mapping of the localized interface and surface states of InGaAs lattice matched to Fe-doped InP by infrared spectroscopy


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(Received 10 April 1992; accepted for publication 2 July 1992)

Infrared absorption and photocurrent measurements have been applied to study the photoresponse below the band gap of indium gallium arsenide (In$_{0.55}$Ga$_{0.47}$As) grown lattice matched to Fe-doped semi-insulating indium phosphide (InP) substrates by various epitaxial growth techniques, including molecular beam epitaxy, liquid phase epitaxy, and metalorganic chemical vapor deposition. It is found that Fe at the InGaAs/InP interface is responsible for exciton-like and polarization sensitive absorption peaks. Both electron and hole emission into the conduction and valence bands, respectively, were observed, and a deep Fe level was identified 0.37 eV below the conduction band edge of bulk Fe:InGaAs. Lowering of the local crystal symmetry due to the interface electric field is proposed to be the mechanism that describes the dipole-allowed interband absorption of 3d transition metal impurities in narrow band gap III-V compounds like the Fe$^{2+}$:InGaAs used in this study. The ambiguity in distinguishing InGaAs quantum well intersubband absorption signals from the Fe interband absorption signals is also addressed.

I. INTRODUCTION

There has been a considerable effort during the past decade to study defects and deep levels at heterojunctions between III-V compound semiconductors. Developing good control of these interface deep levels will govern the ultimate device performance, as well as lead to a thorough understanding of fundamental device physics. Two well known illustrations of the importance of study of deep levels are the observations of EL2 and of DX centers in the GaAs/AlGaAs material system. Though a unified model that can satisfactorily explain all of the experimental data is still lacking, it is none the less agreed that it is nonstoichiometric growth (e.g., As$_{Ga}$), dopant impurities (e.g., Si$_{Ga}$), and their associated complexes that give rise to the deep levels in the GaAs/AlGaAs system.

InGaAs lattice matched to InP is another technologically important material system that has great potential in high speed electronic and optoelectronic device applications. Although many novel device structures have been proposed and great progress has been reported, there are still unresolved issues in this system. In particular, detailed analyses of secondary ion mass spectroscopy (SIMS), optical deep level transient spectroscopy (DLTS), and capacitance-voltage ($C-V$) measurements indicate the existence of deep, localized states at the interface between InGaAs epilayers and Fe:InP substrates and it has been speculated that these states are due to Fe related defects.

The understanding of 3d transition metal impurities in

the wide band gap II-VI and III-V binary compounds is now well established. The observation of strong finger-type interatomic absorption and photoluminescence (PL) at low temperature between the crystal field splitting multiplets ($^3E$, doubly degenerate and $^5T_2$, triply degenerate) is thought to be evidence that transition metal impurities reside in substitutional sites with $T_d$ symmetry. A typical value of the crystal field splitting energy is 3000 cm$^{-1}$ (0.37 eV) for Fe in the wide band gap III-V compounds, the associated first order spin-orbital splitting within the $^3T_2$ excited state multiplets is 300 cm$^{-1}$, and the second order spin-orbital splitting within the $^3E$ ground state multiplets is only 50 cm$^{-1}$. As a more specific example, for Fe in InP it is now well accepted that the $^3E$ Fe$^{2+}$ ground state is 0.63 eV below the InP conduction band edge, the $^5T_2$ Fe$^{2+}$ excited state is 0.35 eV higher than the $^3E$ ground state, and the Fe$^{3+}$ $A_1$ state is 0.71 eV below the $^3E$ ground state and is nearly pinned to the InP valence band edge at room temperature. These levels are illustrated schematically on the left-hand side of Fig. 1.

Recently, Dansa et al. investigated a molecular beam epitaxially (MBE) grown n-In$_{0.55}$Ga$_{0.47}$As/Fe-doped semi-insulating (SI)InP interface and concluded that the Fe impurities are localized at the interface as electron-like traps with an activation energy of 0.32 eV. Kidoguchi et al. also reported the SIMS and DLTS observation of deep levels associated with the segregation of Fe impurities at the interface of liquid phase epitaxially (LPE) grown InGaAsP/Fe:InP junction-field effect transistors (JFETs). The interfacial Fe concentration was found to be three orders of magnitude larger than that contained in the Fe:InP substrate (10$^{15}$ cm$^{-3}$). Loualiche et al. also studied MBE grown Si-doped and undoped In$_{0.55}$Ga$_{0.47}$As epilayers on both Fe-doped SI InP and S-doped n$^+$-InP substrates. A 0.33 eV deep level found at the surface and the

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interface was suggested to be oxygen related. On the other hand, from spectroscopic measurements, Guillot et al. reported a much weaker PL intensity at 0.34 eV in their study of LPE grown Fe-doped InGaAs/n+ InP and suggested that the \( ^3T_2 \) Fe\(^{2+}\) excited state was nearly in resonance with the InGaAs conduction band edge.

In spite of the work mentioned above, it remains true that no directly measured infrared (IR) absorption between the crystal field splitting multiplets of Fe in InGaAs has been reported. There is indeed a great need to understand the optical response below the band gap of InGaAs, especially because of the current interest in novel long wavelength intersubband infrared absorption (LWIR) quantum well detectors based on the InGaAs/Fe:InP system. The purpose of the present work serves (i) to clarify the optical ionization energy of the deep level at the InGaAs/Fe:InP interface and to identify its origin, (ii) to propose a model that consistently explains the polarization sensitive absorption for transition metal impurities at the heterojunction of narrow band gap materials such as the InGaAs:Fe considered in the present study, and (iii) to demonstrate the ambiguity that can arise in identifying and distinguishing the quantum well intersubband absorption signals and the interface Fe interband signals in the InGaAs/Fe:InP material system.

We report here what we believe is the first direct observation of exciton-like infrared absorption due to electron and hole transitions from the Fe\(^{2+}\) 3d deep level to the conduction and valence band edges in InGaAs. The deep Fe levels are present because of the movement of Fe into the InGaAs epilayer from the Fe:InP substrate. The polarization sensitivity of the absorption was found to be strongly dependent on the interface electric field and hence was a function of dopant concentration. Large Stark shifts between TE and TM absorption peaks were also observed. Rehybridization of sp orbitals \((A_1, B_1, B_2, E)\) of d band states \((^3E\) and \(^3T_2)\) due to the lowering of local crystal symmetry in the presence of an interface electric field from \(T_d\) to \(D_{2d}\) will be presented to explain these experimental results.

II. MEASUREMENTS

The samples used in this study are listed in Table I and they include MBE grown doped InGaAs/Fe:InP, with different doping concentrations and epilayer thickness, LPE grown Fe:InGaAs/Fe:InP, and metalorganic chemical vapor deposition (MOCVD) grown undoped InGaAs/undoped InP/Fe:InP. A test set of samples of doped and undoped InAs/InGaAs/AlAs single quantum well (SQW) heterostructures on Fe:InP were also included to facilitate the identification of LWIR signals and interface Fe interband absorption signals. The InGaAs epilayers used for this study were of high crystalline quality; typically the lattice mismatch was less than \(5 \times 10^{-4}\) and the full width at half maximum (FWHM) of (400) double-crystal x-ray diffraction epilayer peaks was less than 28 arc s. Room temperature photoluminescence (PL) measurements indicated the InGaAs band gap to be about 0.74

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe interband transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A MBE grown, n(^+) (10(^{19}) cm(^{-3}))</td>
<td>electron-like at interface</td>
</tr>
<tr>
<td>B MBE grown, undoped</td>
<td>electron- and hole-like at interface</td>
</tr>
<tr>
<td>C LPE grown, Fe doped</td>
<td>electron- and hole-like at interface, bulk, and surface</td>
</tr>
<tr>
<td>D MOCVD grown, undoped</td>
<td>electron- and hole-like at interface</td>
</tr>
<tr>
<td>E MBE grown, doped</td>
<td>electron-like at interface</td>
</tr>
<tr>
<td>InAs/InGaAs/AlAs/InGaAs SQW</td>
<td>QW intersubband transition</td>
</tr>
<tr>
<td>F MBE grown, undoped</td>
<td>electron-like at interface</td>
</tr>
<tr>
<td>InAs/InGaAs/AlAs/InGaAs SQW</td>
<td>QW intersubband transition</td>
</tr>
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eV. The impurity concentration and the sample thickness were also calibrated by the IR plasma absorption and Fabry-Perot measurements, in addition to Hall measurements and profilometry thickness measurements.

Fast Fourier transform infrared spectroscopy (FTIR) was applied to study both the infrared (IR) absorption and the photocurrent response. An IBM-32 FTIR spectrometer with a glowbar source, a mercury cadmium telluride (MCT) detector, and a BaF$_2$-based aluminium wire IR polarizer were used for the measurements and the spectral resolution was 4 cm$^{-1}$. For the photocurrent measurement, 150-nm-thick Cr/Au contact pads were thermally deposited and the electrode spacing ranged from 120 to 5 μm. In the photocurrent measurement scheme, IR light was shone from the backside of the samples and passed between the electrodes to ensure the maximum IR absorption at the InGaAs/InP interface; a double-side polished Fe:InP filter (350 μm thick) was used to avoid any substrate IR conduction. The photocurrent signal from the device was sent back to the FTIR input. For the absorption measurement scheme, in order to increase the absorption strength, samples were first mechanically lapped and then chemical etched (with 1% bromine-methanol solution) to a thickness of 40 μm. Each sample was then sandwiched between a pair of parallel aluminium plates and the IR light was focused upon the cleaved sample edge by a reflection objective. A typical sample size was 3 mm (L) by 2 mm (W). The number of internal reflections was 2 before thinning and increased to 20 after polishing. This pseudo-waveguiding geometry has the following important advantages over the more common Brewster angle and 45° bevel angle configurations: longer optical path, more efficient input coupling (65% of optical power transmission through the cleaved sample edge), excellent polarization purity, and immunity from Fabry-Perot effects. With regard to polarization purity, in the Brewster angle incidence configuration, because of the large index of refraction of semiconductors, over 90% of the refracted electric field inside the semiconductor will lie in the quantum well plane rather than perpendicular to it and the effective electric field component along the growth direction is hence very small. In the 45° bevel angle configuration, rotation of the polarization angle cannot separate its TE and TM components completely because of the natural limitation of this geometry (TE refers to the transverse electric field, for which the electric field is along the x-y plane; while TM refers to the transverse magnetic field, in which the electric field is along the z, i.e., growth direction). In contrast, for electromagnetic waves propagating along the x-y plane as they are in the pseudo-waveguiding geometry, a discrimination ratio of over 40 can be easily achieved for orthogonal polarizations (e.g., TE and TM) using an IR polarizer at the input.

Room temperature transmission and photocurrent measurement data are shown in Figs. 2 through 4. Figure 2 shows the unpolarized absorption spectra for three of the samples listed in Table I; the tentatively assigned absorption peaks are also indicated. Figure 3 illustrates the IR photocurrent response of Fe-doped InGaAs together with its IR absorption data in the spectral range between 4800 cm$^{-1}$ (0.6 eV) and 1500 cm$^{-1}$ (0.18 eV). Figure 4 shows the IR absorption spectra of doped and undoped single quantum well (SQW) samples and doped InGaAs/Fe:InP.

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This figure is included to illustrate the ambiguity that exists in distinguishing the LWIR signal from the Fe interband signals and shows the polarization sensitive absorption peaks associated with the Fe interband signals.

IV. THEORETICAL CONSIDERATION

There is an experimental observation associated with the "metallurgically abrupt" InGaAs/Fe:InP interface that is very important to this work. It is important to note that a thin Fe-rich InP surface segregation region is found to form on the substrate as it is heated during the pregrowth process. A second important experimental observation is that the energy separation of the crystal field splitting levels of a given 3d impurity are likely independent of the specific host crystal for a large number of wide band gap II-VI and III-V binary compound semiconductors. Thus, we assume as a zeroth order approximation that the Fe 3d ($Fe^{3+}A_1;Fe^{2+}E, T_2$) bands are continuous across the InGaAs/InP interface and penetrate a finite length into the InGaAs (say, a few nanometers) due to the outdiffusion of Fe impurities. This assumption leads to the conclusion that the $Fe^{2+}T_2$ excited states reside nearly resonant within the conduction band edge of InGaAs (which is also consistent with the accepted estimate of InGaAs/InP conduction band offset, 0.2 eV). Though Fermi level pinning at semiconductor interfaces and surfaces is a complicated function of charge redistribution, dopant concentration, and surface states, and has been one of the topics of debate in semiconductor physics over the past decades, we assume that the Fermi level within the InP substrate and near the InGaAs/Fe:InP interface is pinned to the $Fe^{2+}E$ level. On the InGaAs surface, we assume it is pinned to the InGaAs surface states, which are 0.2 eV below the InGaAs conduction band edge. 

We further point out the existence of interface and surface depletion regions which (1) introduce strong electric fields and dipole layers, and (2) lower the local crystal symmetry from $T_d$ to $D_{3d}$ at the heterojunction and at the surface.

We proceed by applying group theory to study the Fe electronic states associated with $D_{3d}$ symmetry under a strong interface electric field. The half-filled $Fe^{2+}3d^5$ state has $A_1$ symmetry and lies deep within the valence band of InGaAs and will be neglected. The free ion $Fe^{2+}3d^5$ multiplets ($2D$, with angular momentum $l=2$) will first split into a double degenerate ground state, $^3E$, and a triply degenerate excited state, $^3T_2$, under the global $T_d$ symmetry. Since the experiments were done at room temperature, the second order spin-orbital splitting ($\sim$50 cm$^{-1}$) of the degenerate $^3E$ ground states can be neglected and they can still be treated as degenerate; for convenience the $^3T_2$ excited states can be temporarily treated as degenerate. Then the interface electric field can be turned on and the symmetry lowered down to $D_{3d}$. The degenerate $^3E$ ground states then split into $A_1+B_1$ states (a one-dimensional representation with basis functions $X^2$ and $Y^2$, which are S-like), and the triply degenerate $^3T_2$ excited states split into $B_1+E$ states [with basis functions $Z$ and $(X,Y)$, which are P-like]. This symmetry analysis essentially leads to the description of localized $d$ band states at the interface as a nearly degenerate set of $(S,P)$ atomic orbitals under the influence of a strong interface electric field. Tight binding analysis can then be applied within this $(S,P)$ nearly degenerate set, and clearly one would expect to see a large Stark effect and the hybridization of these atomic orbitals. This then explains the polarization sensitive-absorption and the energy splitting between the TE and TM absorption peaks (Stark effect) seen experimentally. The powerful thing about using such a symmetry argument, is that based on it, one would expect to see both electron-like and hole-like Fe-interband absorption under suitable circumstances. Theoretically this result is reached by grouping together the $(A_1, B_2, E)$ states as an electron nearly degenerate set $(B_2$ and $E$ are resonant within the InGaAs conduction band edge) and grouping $(B_1, X, Y, Z)$ as the hole nearly degenerate set $(X, Y, Z$ are the valence band atomic orbitals of InGaAs). Again a large Stark shift is expected to occur between the TE and TM hole-like interband absorption. Experimentally both electron- and hole-like Fe interband absorption is observed in the undoped InGaAs/Fe:InP and Fe doped InGaAs/Fe:InP samples, and only electron-like interband absorption is found in heavily n-doped InGaAs/Fe:InP samples, because of the phase space filling effect. These dipole allowed interband absorption states are also drawn on the right-side of Fig. 1.

IV. DISCUSSION

A first look at the strong and sharp absorption peaks in Fig. 2 would misleadingly suggest that they are from some unknown optical interference effects which also mysteriously incorporate the polarization effect. However, the
photocurrent measurement data certainly verify that these are electronic state transitions. The reason that such extremely sharp absorption peaks are seen even at room temperature comes not only because they involve atomic state transitions, but also because of the lower dimensionality (1D); an analogue is found in quantum well and quantum wire exciton absorption.

The assignments of these absorption peaks are also listed in Table I. To briefly summarize, the absorption peak at 2500 cm\(^{-1}\) seen in the MBE samples is assigned to an electron-like interband transition from Fe\(^{2+}\)\(^\cdot\)\(^2\)E to the InGaAs conduction band edge at the InGaAs/InP interface, while the peak at 3900 cm\(^{-1}\) is suggested to be the hole-like interband transition from the InGaAs valence band edge to Fe\(^{2+}\)\(^\cdot\)\(^2\)E. This can be easily seen from Figs. 2(a) (n\(^+\)-InGaAs), 2(b) (undoped InGaAs), and 2(c) (Fe-doped InGaAs). The small spikes located at the higher energy sides of these absorption peaks are consistently found in the MBE samples and are suggested to be related to the local vibration modes. The additional feature seen in LPE-grown Fe-doped InGaAs at 1700 cm\(^{-1}\) and 4600 cm\(^{-1}\) is assigned to be electron- and hole-like Fe interband transitions, respectively, at the air-InGaAs surface, where it is assumed that the Fermi level is pinned to the Fe\(^{2+}\)\(^\cdot\)\(^2\)E at the surface, while the main absorption centered at 3000 cm\(^{-1}\) is assigned to be Fe in the midgap of InGaAs. The identification of this Fe 3000 cm\(^{-1}\) absorption peak agrees well with a recent low temperature PL study of LPE-grown Fe:InGaAs.\(^6\)

Figure 3(b) (lower panel) shows the absorption data of LPE-grown Fe-doped InGaAs and Fig. 3(a) (upper panel) shows its photocurrent response (the electrode spacings are 5 and 10 \(\mu\)m). The excellent agreement between these absorption and photocurrent peaks again proves that the Fe level interband transition is responsible for the below bandgap absorption of InGaAs/Fe:InP in this study.

Interface absorption due to Fe was also observed in MOCVD samples in which a thin epilayer of undoped InP (100 nm) had been inserted between the Fe:InP substrates and the InGaAs epilayer. This observation is consistent with our model because Fe is known to diffuse quickly through InP epilayers grown on Fe:InP substrates, and has been observed using SIMS by Holmes et al.\(^11\) for LPE grown samples and by Knight et al.\(^12\) for low pressure MOCVD grown samples.

Two factors affect the overall photocurrent response curve: (1) the blackbody source (glowbar) intensity is not constant over the wide spectral range studied here, and (2) the fast surface and interface recombination speeds can easily obscure the photocurrent response curve because of the ultra short free carrier lifetime in the presence of a large density of antisite defects.\(^16,17\) Figure 4(b) (lower panel) demonstrates the polarization sensitive absorption at the interface of n\(^+\) InGaAs/Fe:InP and clearly indicates a large Stark shift (50 meV) between TE and TM absorption peaks. Due to the unequal power loss for TM and TE light propagating in an imperfect conducting parallel plates, the unpolarized light absorption data seems to favor the TE absorption because of the dominant loss of TM mode. However, the excellent polarization selectivity of the pseudo-waveguiding geometry clearly reveals the equal absorption strength for the different polarizations and the energy shift between TM and TE (TM always has a higher absorption energy when compared with TE), which again proves the validity of the proposed model. Figure 4(a) (upper panel) displays the unpolarized absorption data of a doped SQW, undoped SQW, and n\(^+\) InGaAs/Fe:InP. These 3 samples were from the same growth period and had exactly the same structures, except that the first one included a doped InAs/InGaAs/AlAs SQW,\(^14\) the second one had an undoped SQW, and the last one did not have any quantum well. It is clear that the Fe interband electron-like absorption is reproducible from sample to sample and the LWIR quantum well signal could be easily misidentified if one was not aware of the Fe interband absorption. Access to specially designed test heterostructures is essential to being able to identify the various peaks.

Although a full scale analysis of the mutual interaction between the crystal field and interface electric field, and their effects on the interface Fe states is beyond the scope of this article, it is none the less possible to see the trends in the relative Stark shift between TE and TM absorption peaks and the absolute absorption energy shift in differently doped samples, basically follow the predictions of the tight binding analysis. It can be seen that for heavily doped n\(^+\) InGaAs/Fe:InP (10\(^{19}\) cm\(^{-3}\)), only the electron-like Fe interband absorption is allowed (because of the phase space filling effect). This transition has the largest Stark splitting (400 cm\(^{-1}\), 50 meV) and higher interband absorption energy because of the stronger interface electric field. For the undoped InGaAs/Fe:InP (10\(^{15}\) cm\(^{-3}\)), both the electron- and hole-like Fe interband transitions are allowed but the Stark shift is only 200 cm\(^{-1}\). An estimate of the interface electric field strength from the Stark shift gives a number around 10\(^5\) V/cm, which has been recently verified by Zhou et al.\(^15\)

V. CONCLUSION

Based upon the above analysis, and the observation of strong interband electron- and hole-like absorption, and a large Stark shift between the TM and TE absorption peaks, it can be concluded that these absorption peaks originate from the finite outdiffusion of Fe impurities into the InGaAs epilayer in the vicinity of InGaAs/Fe:InP interface. Optical data for the bulk Fe\(^{2+}\) to conduction edge transition energy (3000 cm\(^{-1}\), 0.37 eV) agree well with the previously published data. The existence of these absorption peaks means that caution must be exercised to distinguish quantum well LWIR absorption from the Fe interband absorption.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation, Grant ECS 9008485. The authors wish to thank Professor R. Reif at MIT for offering the use of his
FTIR facility, and Professor R. Jones at Harvard University for helpful discussions.