Field effect on electron emission from the deep Ti donor level in InP

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The effect of electric field on the thermal emission of electrons from the Ti^{3+}/Ti^{4+} deep donor level in InP has been investigated. Double-correlation deep-level transient spectroscopy as well as differential-isothermal-capacitance transient measurements have been carried out on low-pressure–metalorganic-chemical-vapor-deposition-grown InP:Ti samples. It is found that the emission rates are strongly field dependent increasing by up to a factor of 17 corresponding to an increase of the field by a factor of 3.5 in the measured temperature range of 260 to 340 K. The experimental data are well fitted with a Poole-Frenkel model employing a three-dimensional square-well potential associated with the Ti^{3+}/Ti^{4+} level with a radius $r=4.6$ nm. The fit of this model to the experimental data yields variations in the activation energy, $\Delta E=0.48\pm0.02$ eV to 0.57 ± 0.02 eV, depending upon the actual field strength. An extrapolated zero-field $\Delta E(0)=E_C-E_T=0.59\pm0.02$ eV is found. The electron-capture cross section is determined to be $\approx(6.6\pm0.3)\times10^{-13}$ cm^2. Thus, the controversy about the previously reported variations in ΔE values is resolved. A comparison of $\Delta E(0)$ with the Ti^{3+}/Ti^{4+} energy position in GaAs and $In_{0.53}Ga_{0.47}As$ shows that the energies are within 20 meV horizontally across the heterojunction, confirming a prediction of the "internal-reference" rule for the energy position of transition-metal levels in isoelectronic semiconductors.

I. INTRODUCTION

Doping of InP with Ti results in an electronic level around the middle of the band gap. This is generally accepted to be the Ti^{3+}/Ti^{4+} donor level. Ti doping is presently supposed to offer the potential of rendering slightly *p*-doped material semi-insulating.[1] Ti is much superior to Fe, a deep acceptor able to compensate *n*-type material, from the point of view of thermal stability.[2]

Our present study was partly motivated by the fact that although a number of studies[3-9] have been devoted to understand the physical properties of the Ti^{3+}/Ti^{4+} donor, its energy position in the band gap of InP remains very controversial. In particular, the activation energy ($\Delta E=E_C-E_T$) determined by different groups using the same technique of deep-level transient spectroscopy (DLTS) differs considerably from 0.54 ± 0.03 eV to 0.63 ± 0.03 eV. A closer look at these reports reveals that the largest activation energy[8] (0.63 ± 0.03 eV) was obtained in samples with the lowest background electron concentration of 5×10^{15} cm^{-3} while the lowest value[7] (0.54 ± 0.03 eV) was obtained in samples with the highest donor concentration of $1-3\times10^{17}$ cm^{-3}. In some preliminary investigations we also observed a large variation in DLTS activation energy of the InP:Ti level from sample to sample containing different shallow-donor concentrations. For some samples with a large shallow-donor concentration, the activation energy was found to be as low as 0.48 eV. This trend suggests that the thermal electron emission is strongly influenced by the electric field present in the space-charge region, lowering the barrier for electron emission in material with large donor concentration (large junction field). We have, therefore, investigated the influence of the electric field on electron emission from the Ti level in InP. We find that all previous data can be reconciled after the field effect is properly taken into account. In addition, a recent proposal[10] on the invariance of transition-metal energy-level positions (like Ti^{3+}/Ti^{4+} and Fe^{2+}/Fe^{3+}) across heterojunctions like $InP/In_{0.53}Ga_{0.47}As$ can now be more closely probed than done hitherto.[11,12]

II. EXPERIMENTAL

n-type Ti-doped InP epitaxial layers were grown using low-pressure–metalorganic-chemical-vapor deposition (LP-MOCVD) on n^+-type InP:Sn substrates. The epilayers were co-doped with Si as shallow donors. The details of the epitaxial growth have been reported elsewhere.[13]

For space-charge measurements, p^+-n junctions were fabricated on the MOCVD epilayer by zinc diffusion to make p^+-type layers and simultaneously providing Zn-Au Ohmic contacts to these top layers in a way similar to that reported in Ref. 14. The details of this p^+-n junction fabrication technique are being published elsewhere.[15]

The measurement of thermal-emission rates was carried out with a high-sensitivity capacitance bridge built in our laboratory similar to the one described in Ref. 16. The system is computer controlled and the entire capacitance transients generated by filling pulses are stored for analysis. These data can be used for the synthesis of conventional DLTS spectra by subtracting capacitance values at two different delay times t_1 and t_2 and plotting this difference ΔC as a function of temperature. The re-

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sult is equivalent to the double boxcar integrator method. The system can also be used for direct determination of emission time constants by taking isothermal transients.

Capacitance-voltage (*C-V*) measurements were carried out using a Boonton 76A capacitance meter, to determine the shallow-donor concentration and compute the electric-field values within the junction space-charge region.

III. EXPERIMENTAL RESULTS AND ANALYSIS

The electric field in the space-charge region of a *p-n* junction continuously varies from maximum at the junction to zero at the edge of the space-charge region. The usual capacitance transient measurements, therefore, cannot be used for a precise determination of the emission rate from a trap if the rate is field dependent. Instead, differential capacitance measurements have to be carried out in which the charge-carrier emission from a deep level is observed for a small portion of the space-charge region where the variation of the electric field can be neglected since it is small. For the initial detection of the field dependence of the emission rate we used our DLTS system in a mode which is equivalent to the double correlation DLTS technique.[17] In this experiment a temperature scan was carried out in which capacitance transients were recorded for two filling pulses varying slightly in pulse height. The computer then subtracted the two transients for each temperature and a boxcar spectrum was generated from the set of difference transients.

Figure 1 shows the double correlation DLTS spectra for the same rate window for two different field values at a reverse bias $V_R = -3$ V. As is typical for the field enhancement of emission rates, the DLTS peak with higher field occurs at lower temperature than the one with lower field showing that the electron-emission rates from the Ti level are enhanced with an increase in electric field.

Although the electric-field dependence can be derived from such DLTS measurements, a better method is to compute the emission rates directly from full isothermal capacitance transients by a difference method.[18] Compared to DLTS, this method not only gives the emission rates directly but also a better temperature stability is assured (in DLTS temperature scans are taken). In these measurements the sample was held at a fixed temperature (the temperature stability of our cryostat was better than ± 0.5 K). The capacitance transients following a filling pulse were measured at a reverse bias of -3 V. The experiment was repeated 992 times and the computer averaged over these transients to reduce noise. Two such averaged transients taken at slightly different pulse heights were subtracted to give the emission rate from a small portion of the space-charge region. Figure 2 shows two such transients and their difference plotted on logarithmic scale to obtain the emission time constant and hence the emission rate. The linearity of the differential transient on a logarithmic scale suggests negligible variation of the field in the test zone of the space-charge region. The field in this zone was calculated from the *C-V* data measured at the same temperature taking into account the λ distance[19] (crossover point of the Fermi level with the deep-level position). The field variation in the test zone was always less than 10% of the actual field value.

To obtain emission rates over a large variation in field, two kinds of diodes were employed. The shallow-donor concentration, obtained from *C-V* analysis, was 3.5×10^{16} cm^{-3} for the low-field samples and 1.5×10^{17} cm^{-3} for the high-field samples. The Ti level concentration was 7×10^{15} cm^{-3} and 5×10^{16} cm^{-3}, respectively, for the two. The ratio $\Delta C/C$ of peak capacitance variation to the equilibrium capacitance was less than 0.1 in all cases.

The electric-field dependence of electron-emission rates from the Ti level in InP thus obtained at various temperatures is shown in Fig. 3. The limitations on the temperature range investigated were the response time of the system (limited, in our case, mainly by the filter used) for the fastest transients possible to record and in the lower

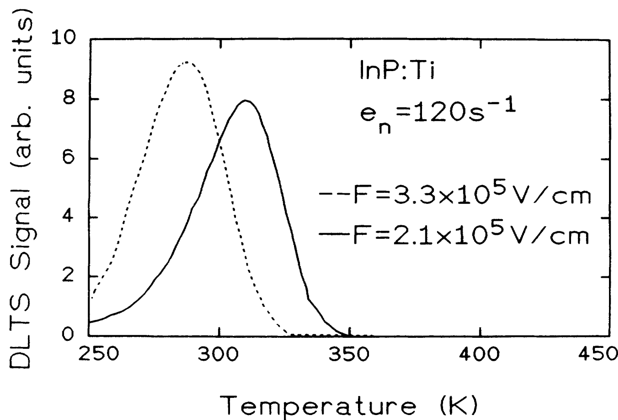

FIG. 1. Double-correlation DLTS spectra of the Ti level in InP for the same rate window at two different electric fields *F*. $V_R = 3$ V.

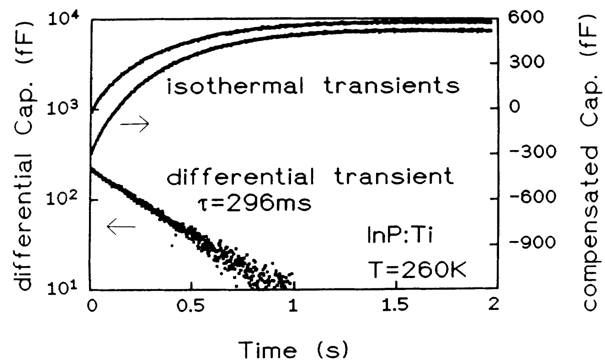

FIG. 2. Two isothermal capacitance transients (linear scale) at reverse bias of -3 V obtained by applying pulses of 1.5- and 1.2-V height. The difference (taken point by point) between the two transients is plotted on a logarithmic scale. The average field in the emission volume of the space-charge region for the differential transient is 2.4×10^5 V/cm. The emission time constant $\tau = 1/e_n$.

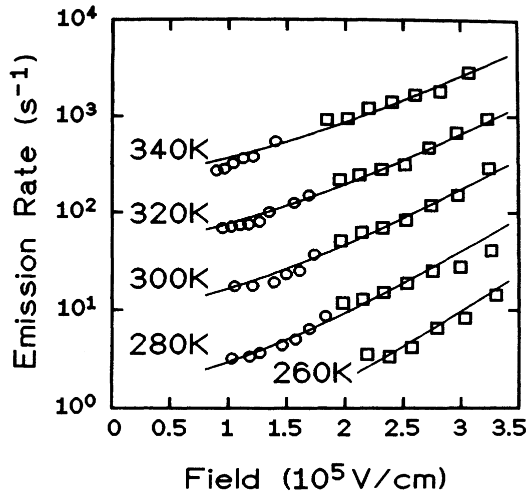

FIG. 3. Electric-field dependence of electron-emission rates from the Ti^{3+}/Ti^{4+} level in InP at different temperatures. Squares and circles: experimental values for two different samples having shallow-donor concentrations of 3.5×10^{16} cm^{-3} (circles) and 1.5×10^{17} cm^{-3} (squares), respectively; curves: theoretical fit with the Poole-Frenkel model using a three-dimensional square-well potential of radius 4.6 nm.

temperature range the necessity for the transients to saturate within the time window available. As seen from Fig. 3, the electron-emission rate shows a strong field dependence. Upon an increase of the field by a factor of 3.5, e_n increases by a factor of 17.

IV. THEORETICAL ANALYSIS AND DISCUSSION

A. The deep Ti donor

There are two basic mechanisms known for the enhancement of emission rates from a deep level due to the junction electric field. The first is the lowering of the defect potential barrier due to the field known as the Poole-Frenkel effect and the second the phonon-assisted tunneling of electrons and/or holes from the defect potential to the conduction and/or valence band. The phonon-assisted tunneling results in a strong enhancement of emission rates,[18,20] increasing by many orders of magnitude for a threefold increase in the electric field. The moderate field enhancement of the kind observed in the present case of InP:Ti is typical of the Poole-Frenkel effect.[21,22] In addition, Irmscher *et al.*[22] have considered the validity of the application of the phonon-assisted tunneling model to charged centers (the model having been successfully applied to neutral centers) and have come to the conclusion that only the usual Poole-Frenkel model is applicable to deep-charge centers. Thus, we have analyzed our data employing the Poole-Frenkel model of the electric-field enhancement of emission rates.

The Poole-Frenkel barrier lowering has been modeled for various possible defect potentials.[23] Since the Ti level in InP is supposed to be a donor level, for electron emission from this level the Coulombic potential model was our first choice. The emission rate at field F, according to this model is given by

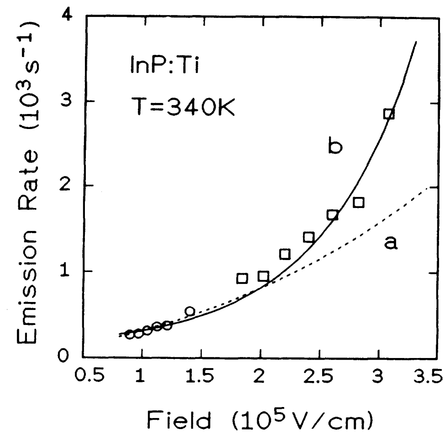

FIG. 4. Electric-field dependence of electron-emission rates according to the Poole-Frenkel model (curves) compared with experimental values (squares and circles for two different samples): (a) the three-dimensional Coulombic potential and (b) the three-dimensional square-well potential with $r=4.6$ nm.

$$\frac{e_n(F)}{e_n(0)}=\frac{1}{\gamma^2}[e^{\gamma}(\gamma-1)+1]+\frac{1}{2}\ , \tag{1}$$

with

$$\gamma=(qF/\pi\epsilon_r\epsilon_0)^{1/2}q/kT\ , \tag{2}$$

where q is the electronic charge, ϵ_0 the permitivity of free space, ϵ_r the relative permitivity of the host crystal, k the Boltzmann constant, T the temperature, and F the electric field. Figure 4 shows the result of applying this mod-

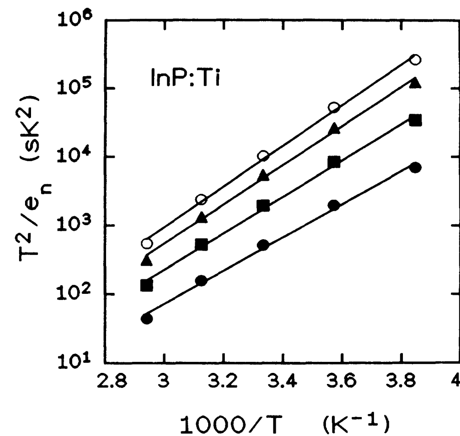

FIG. 5. Arrenius plot of electron-emission rates from the Ti level in InP at constant electric fields obtained from the best fit curves of Fig. 3. Filled circles: $F=3\times10^5$ V/cm, $\Delta E=(0.48\pm0.02)$ eV. Squares: $F=2\times10^5$ V/cm, $\Delta E=(0.53\pm0.02)$ eV. Triangles: $F=1\times10^5$ V/cm, $\Delta E=(0.57\pm0.02)$ eV. Empty circles: extrapolated $F=0$, $\Delta E=(0.59\pm0.02)$ eV.

el (dashed line). It is obvious that the Coulomb potential yields a much weaker field dependence than experimentally observed. Another possibility is a screened Coulombic potential. Such a potential gives an even weaker field dependence than the pure Coulombic model[23] and hence would not fit our data.

If the impurity potential is of square-well type, the emission rate at field F is given by[23]

$$\frac{e_n(F)}{e_n(0)}=\frac{1}{2\gamma}(e^{\gamma}-1)+\tfrac{1}{2}\ , \tag{3}$$

where, in this case

$$\gamma=qFr/kT\ , \tag{4}$$

r being the radius of the three-dimensional square well. In this case r and $e_n(0)$ are free parameters. It was found that using $r=4.6$ nm (3) and (4) agree well with the experimental data at all temperatures of measurement as seen in Figs. 3 and 4.

From the theoretical fit curves of Fig. 3, electron-emission rates at constant field values can be obtained. Arrhenius plots then give the activation energies at these fields. We have obtained emission rates at different fixed field values from $F=0$ to 4×10^5 V/cm and obtained activation energies ΔE from them. Figure 5 shows the Arrhenius plot at three field values $(3,2,1)\times10^5$ V/cm lying within our measurement range as well as at the extrapolated zero field. The activation energies obtained from this plot are $\Delta E=(0.48,\ 0.53,\ 0.57,\ 0.59)\pm0.02$ eV, respectively.

The activation-energy variation with electric field obtained in this manner is shown in Fig. 6. The filled symbols in this figure correspond to the values that lie in our experimental data range. The observed variation in ΔE covers the different previously published values[3,4,7,8] as well as those obtained in our preliminary DLTS studies using single pulse experiments.

Our fit value of r for the square-well potential also enables us to model the electron-capture cross section σ_n for the Ti donor level in InP. The cross section corresponding to the square-well radius $r=4.6$nm is $(6.6\pm0.3)\times10^{-13}$ cm^2. This value is in agreement with the observation[8] that the electron-capture cross section of this level is too large to be measured directly by varying the filling pulse widths [the extrapolated σ_n $(1/T=0)$ value reported in literature[4,7,8] varies from 4×10^{-15} to 1×10^{-14} cm^2]

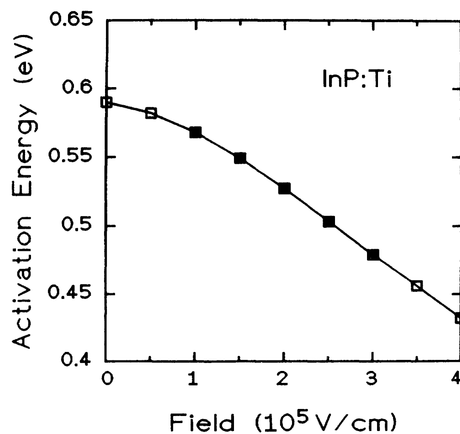

FIG. 6. Variation of electron activation energy from the Ti level in InP according to the Poole-Frenkel model with a three-dimensional square-well potential with $r=4.6$ nm and $e_n(0)$ filled to the data of Fig. 3. The fitted symbols indicate the values lying within our experimental data range.

B. The internal reference rule for heterojunctions

Recently we have determined the energy positions of the Ti^{3+}/Ti^{4+} level in $In_{0.53}Ga_{0.47}As$ (Ref. 11) and GaAs.[24] Now having obtained the field dependence of the Ti^{3+}/Ti^{4+} level in InP and the zero-field energy $\Delta E(0)=0.59$ eV we are in a better position than hitherto of probing whether Ti obeys the "internal reference" rule[10] which implies that the energy position of Ti^{3+}/Ti^{4+} level with respect to an internal reference energy is independent of the host material for isoelectronic semiconductors. The present data on the Ti donor energy position refer essentially to 300 K. The 300-K activation energy of the Ti^{3+}/Ti^{4+} level was found to be 0.37 eV (Ref. 11) in $In_{0.53}Ga_{0.47}As$ and 0.87 eV (Ref. 24) in GaAs with respect to the conduction band. If one assumes that the Ti^{3+}/Ti^{4+} level in these two materials has a similar electric-field dependence of energy to that found for InP in the present investigation then the results of Fig. 6 can be applied to these materials as well. We have evaluated the average fields in the emission volumes for the measurements reported in Refs. 11 and 24 to be 0.15×10^5 V/cm and 0.23×10^5 V/cm, respectively. Comparing with Fig. 6 we expect negligible change in energy for the Ti^{3+}/Ti^{4+} level in $In_{0.53}Ga_{0.47}As$ as well as GaAs.

Figure 7 shows the band diagram of a $GaAs/In_{0.53}Ga_{0.47}As/InP$ heterostructure based upon the internal reference rule of the invariance of the energy position of the Ti^{3+}/Ti^{4+} level in the three semiconductors. The band-gap-discontinuity between InP and $In_{0.53}Ga_{0.47}As$ resulting from this is 0.22 ± 0.02 eV which agrees with the generally accepted value[25] of 0.25 ± 0.01 eV within experimental error. The relative positions of

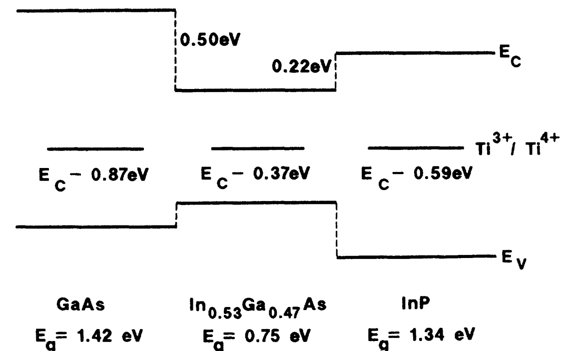

FIG. 7. Deep titanium donor level in GaAs, $In_{0.53}Ga_{0.47}As$, and InP at 300 K according to the internal reference rule.

conduction-band edges of GaAs and InP (0.28 eV) is also in agreement with the expected value.[10] Thus, Ti obviously obeys the internal reference rule.

V. CONCLUSIONS

We have carried out measurements of the electron-emission rates of the Ti^{3+}/Ti^{4+} level in InP as a function of the junction electric field at temperatures ranging from 260 to 340 K using differential capacitance transient techniques (both DLTS and isothermal measurements). We observed a pronounced enhancement of the emission rate with an increase in the electric field. The experimental data fit well with a three-dimensional square-well potential model of radius $r=4.6$ nm giving $\Delta E(0)=0.59\pm0.02$ eV and $\sigma_n=(6.6\pm0.3)\times10^{-13}$ cm^2.

Expecting a similar electric-field effect for the Ti^{3+}/Ti^{4+} level in GaAs and $In_{0.53}Ga_{0.47}As$, the zero-field energy depth of this level in these two semiconductors was calculated using our previously published data. It was found that the Ti^{3+}/Ti^{4+} level obeyed the internal reference rule[10] for the energy position of transition-metals level in isoelectronic semiconductors.

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