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# Annealing study of the electron-irradiation-induced defects $H_4$ and $E_{11}$ in InP: Defect transformation $(H_4\text{-}E_{11})\rightarrow H'_4$

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Capacitance spectroscopy has been used to study the two dominant deep levels, $H_4$ and $E_{11}$, produced in InP by low-energy electron irradiation. The annealing rates of $H_4$ and $E_{11}$ in the $p$-type material are found to be identical, as is also the dependence on free-carrier recombination and on the chemical nature of the acceptor (Cd or Zn). Recombination-enhanced annealing converts these traps to a hole trap $H'_4$, which is not detectable by conventional deep-level transient spectroscopy. Its emission and capture properties are measured and analyzed. The similarity of the creation and annealing behavior of $H_4$ and $E_{11}$ shows that they share a common point defect. Our results lead to the tentative identification of the defect as a phosphorous vacancy-acceptor complex and we show how this may anneal to the $H'_4$ center.

## I. INTRODUCTION

Even though the study of electron-irradiation-induced defects (EIID's) in InP is far less extensive than in GaAs, the corresponding hole and electron traps were classified a few years ago. An initial picture of defect formation and defect reactions has begun to emerge,[1-12] but it needs to be clarified and confirmed by complementary experimental work.

The experiments described in the present paper were conducted with the aim of testing the hypothesis that the two main EIID's, the hole trap $H_4$ in $p$-type InP and the electron trap $E_{11}$ in $n$-type InP, result from strongly correlated microscopic defects having some common point defect. This hypothesis was raised by Sibille and co-workers,[1] who first demonstrated that $H_4$ and $E_{11}$ are both generated by the primary electron collision in the phosphorus sublattice[2] and also observed that their above room-temperature (RT) annealing kinetics are identical,[3] whether measured in the hole or electron-free state and in $p$- or $n$-type material.

To allow a more direct and more reliable comparison we studied the annealing of $H_4$ and $E_{11}$ at the same time in a single $p$-type sample in which the minority-carrier trap $E_{11}$ was expected to exist. The annealing out of the majority-carrier trap $H_4$ is observed by deep-level transient spectroscopy (DLTS), while optical filling and thermal emptying (ODLTS) are used for the minority-carrier trap $E_{11}$.

The results confirm the strong correlation of these two dominant EIID's and also reveal that, in the case of Zn doping, the simultaneous annealing of $H_4$ and $E_{11}$ generates another hole trap that has already been briefly described in a previous communication[4] and labeled $H'_4$. This hole level $H'_4$, generated by a local-defect transformation, has very specific weak-hole-capture properties which make it undetectable in the usual DLTS experiment.

The defect transformation $(H_4\text{-}E_{11})\rightarrow H'_4$ is strongly enchanced by the recombination of free carriers, recombination-enhanced defect reaction (REDR) mechanism, with an approximate 0.3 output efficiency. This excludes a long-range diffusion process followed by retrapping on randomly distributed defects or impurities. The identity of the behavior of the annealing kinetics of $H_4$ and $E_{11}$ is observed here as well as in pure thermal treatments as under stimulation by electron injection. This is a strong indication that these two electronic levels correspond to the same microscopic [$D$(P)-acceptor] complex which is tentatively identified as a $(V_{\rm P}\text{-}A^-)$ pair.

The paper is organized as follows. In Sec. II we review briefly the literature on the creation, the annealing properties, and the physical characteristics of the two dominant EIID's in InP, $H_4$ and $E_{11}$. Experimental details are briefly exposed in Sec. III. Section IV concerns the simultaneous annealing of $(H_4\text{-}E_{11})$ in Zn- and Cd-doped $p$-type InP. The physical characteristics of the thermally generated hole trap $H'_4$ are described in Sec. V and phenomenologically explained with the help of a one-dimensional configuration-coordinate diagram (CCD). The local-defect transformation $(H_4\text{-}E_{11})\rightarrow H'_4$ is discussed in Sec. VI and a responsible microscopic defect is tentatively identified. The main results and conclusions are summarized in Sec. VII.

## II. REVIEW OF THE EIID's $H_4$ AND $E_{11}$ IN InP

The generation and annealing properties of the hole trap $H_4$ in $p$-type InP ($E_a=0.37$ eV, $\sigma_a=8.10^{-16}$ cm$^2$) have been extensively studied in France by the CNET group,[1-7] and in Japan by the NTT group.[7-10] It was first demonstrated by Sibille and co-workers that $H_4$ is produced by the selective displacement of the $P_{31}$ host atom during the initial incoming electron collision and not by the displacement of the heavier $\mathrm{In}_{115}$ atom. This was done by comparing the differential threshold energies of the production rates of many EIID's and also by comparing the creation efficiencies along the (111) and the $(\bar{1}\,\bar{1}\,\bar{1})$ crystallographic directions which favor either the P or the In ejection to the interstitial site.[2]

At the same time it was soon realized by these authors[5] that $H_4$ is not a simple intrinsic defect but a complex involving the $p$-type doping impurity. The experimental demonstration of the complex character of the $H_4$ defect is rather indirect since its physical properties, thermal and optical hole emission rates, do not depend on the acceptor species, Zn or Cd, and since the RT stable concentration $[H_4]$ attained for a given fluence is not clearly related to the doping level. Actually its complex nature was inferred from the occurrence of secondary defect reactions following 25-K electron irradiation and from small differences between the annealing kinetics in Zn- and Cd-doped crystals.[6] Heating at 300 K after low-temperature (LT) irradiation results in a noticeable increase of $H_4$ concentration which is thus created by thermally activated secondary reactions (stage I). It has also been observed[6] that the above RT annealing of $H_4$ in a purely thermal process (stage II) and of three other deep levels, labeled $H_2$, $H_3$, and $E_{11}$, are identical and exactly first order with Cd doping and not quite first order with Zn doping, with an effective frequency,

$$\frac{1}{[D]}\frac{d[D]}{dt}=K(T)=2\times10^{15}\exp\left[-\frac{1.32\ \text{eV}}{kT}\right].$$

The high value of the pre-exponential factor shows that the annealing rates are dominated by a local reaction and the common 1.32-eV value of the activation energy that the atomic event concerned is the same for the whole group of defects. To account for the stage-I reactions following low-temperature irradiation and the stage-II annealing out, they proposed that the defects are $[D(\text{P})\text{-}A^-]$ complexes, where $D(\text{P})$ is either $V_\text{P}$ or $\text{P}_i$. However, the local character of the dominant annealing process is questioned by the work of Yamaguchi and Ando,[7] who observed strong doping impurity effects on the creation efficiency and on the annealing rates of $H_4$ and $H_5$ in Zn-doped $p$-type InP irradiated with 1-MeV electrons or $\gamma$ rays.[8–10] For these authors, $H_4$ has first-order annealing kinetics in the Zn-doped material but with an effective frequency $K$ proportional to the $\frac{2}{3}$ power of the Zn doping level. They assign this sensitivity to the Zn content to a simultaneous generation of $H_5$ by association of a released constituent of $H_4$ to the acceptor. However, the identification of the $\gamma$-ray-induced levels with $H_4$ and $H_5$ seems questionable and the reason for this apparent correlation between the annealing of $H_4$ and the increase of $H_5$ is far from clear, since it has been established that $H_5$ is a complex defect originating in the In sublattice,[11] while $H_4$ originates in the P sublattice. Obviously additional experiments are desirable.

The electron trap $E_{11}$ ($E_a=0.72$ eV, $\sigma_a=2.10^{-13}$ cm$^2$) has until now only been observed by capacitance technique in $n$-type material with $p^+$-$n$ junctions but not in devices with Schottky barriers.[12,13]

From this Benton *et al.*[12] first speculated that $E_{11}$ ($E_{10}$ in their paper) is a complex defect resulting from an interaction between a primitive irradiation damage and another defect introduced during the $p^+$-$n$ junction preparation procedure.

Later it was demonstrated[13] that the primitive radiation damage occurs on the P sublattice and that $E_{11}$ results from a secondary reaction with the acceptors in the $p^+$ region. This was shown by the strong spatial dependence of the frequency of its first-order annealing kinetics,

$$K_{(T)}=-\frac{1}{[E_{11}]}\frac{d[E_{11}]}{dt},$$

in the $p^+$-$n$ junction. This frequency decreases towards the $p^+$ side where the dissociation of the complex defect responsible for $E_{11}$, $[D(\text{P})-S_{11}]$, is more efficiently counterbalanced by the recapture event $D(\text{P})+S_{11}\rightarrow E_{11}$.

To close this review it is worth noting that (1) the annealing of $H_4$ and $E_{11}$ is charge-state dependent (see Table I), and exactly identical in their respective hole and electron empty states, and (2) the annealing of both $H_4$ and $E_{11}$ is stimulated by minority-carrier injection (electron injection for $H_4$ and hole injection for $E_{11}$), and a detailed analysis of this recombination-enhanced defect reaction has been given.[14]

## III. EXPERIMENTAL DETAILS

Some of the samples used in this work were evaporated Ti-Au Schottky barriers on $p$-type InP [Czochralski Zn-doped or Cd-doped liquid-phase-epitaxy (LPE) layers]. Most samples, however, were LPE Zn-doped $p^+$-$p$-$n^+$ junctions with $p\sim1\times10^{16}$ cm$^{-3}$. RT irradiation, with incident-electron energies ranging from 300 keV to 1 MeV, were performed on a Van de Graff accelerator at low current densities (1 $\mu$A cm$^{-2}$) and electron doses ranging from $10^{13}$ to $10^{16}$ $e$ cm$^{-2}$.

The ODLTS and DLOS data were obtained with the double-grating monochromator system described previously.[15] The incident photon energy uncertainty is approximately 20 meV.

Direct-capture cross-section measurements of $H_4'$ were made by partial refilling. The available range of temperature was increased towards the LT side by using optical emptying below 150 K. The unusually large values of the capture time $\tau_c$, greater than 100 s at 120 K, required a specific experimental protocol and its exponential increase with decreasing temperature restricted the available domain to $T>110$ K.

## IV. ANNEALING OF $H_4$ AND $E_{11}$ IN $p$-TYPE InP

### A. Trap identification

Typical DLTS and ODLTS spectra of an $n^+$-$p$, Zn-doped InP junction, irradiated at 1 MeV at RT, are shown in Fig. 1. The majority-carrier traps $H_4$ and $H_5$ are those usually observed in the $p$-type material while the ODLTS reveals two minority-carrier traps. The shallower one, labeled $EP_1$ and occurring near 120 K, is not an EIID since it is also observed in unirradiated samples. The deeper one, $EP_2$ around $\sim270$ K, is only observed in irradiated samples and is identified with the level $E_{11}$ in $n$-type InP by the near identity of their electron emission rates. The ODLTS signature of $EP_2$ in the $p$-type material is

$$E_a = 0.70\ \text{eV},\quad \sigma_a = 1.10^{-13}\ \text{cm}^2\ ,$$

while the averaged published data on $E_{11}$ obtained by DLTS in $n$-type samples is

$$E_a = 0.72\ \text{eV},\quad \sigma_a = 2.10^{-13}\ \text{cm}^2\ .$$

This identification of $EP_2$ with $E_{11}$ is fully buttressed by the identity of their creation properties shown in Fig. 2. It is thus clearly established for the first time that the level $E_{11}$, which acts as an electron trap in $n$-type InP, is also generated in $p$-type material by electron irradiation.

By changing the forward pulse duration in the DLTS experiments from 0.5 ms to 4 s, one observes in Fig. 3(a) a slight increase of the peak attributed to $H_4$ and a concomitant shift towards higher temperatures. This reveals that there exists an unresolved hole trap, with a smaller concentration than $H_4$ and a nearly identical hole emission time, but with a much weaker hole-capture cross section. This level, labeled $H_4'$, is fully resolved after heating the sample during 75 h at 110 °C [see Fig. 3(b)], which totally erases the signal due to the faster capturing level $H_4$.

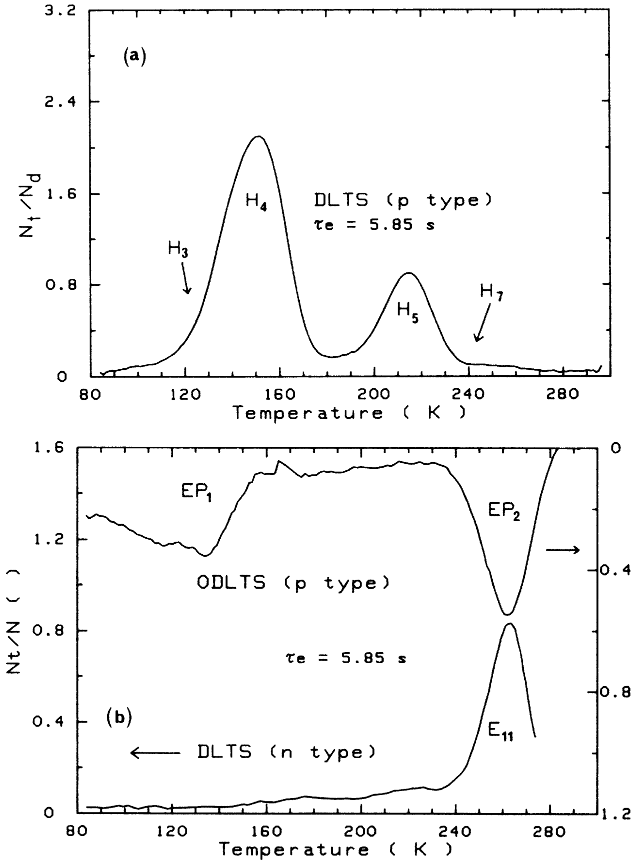

FIG. 1. (a) DLTS spectrum of an $n^+$-$p$ InP irradiated junction. The hole traps are labeled in agreement with Refs. 3 and 5. (b) Direct comparison of the electron emission rates of the minority carrier trap $EP_2$, observed by ODLTS in an $n^+$-$p$ junction, and of the level $E_{11}$ observed by DLTS in a $p^+$-$n$ junction. $N$ is either the acceptor concentration $N_a$ or the donor concentration $N_d$.

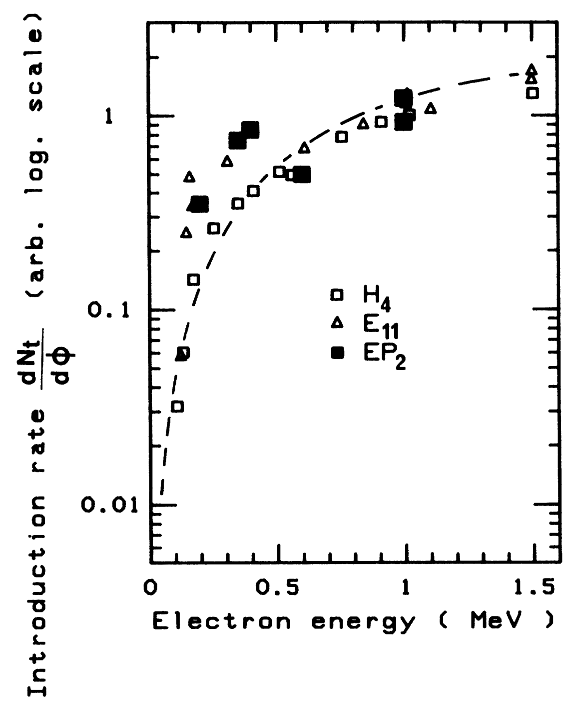

FIG. 2. Introduction rates of the level $E_{11}$ in the $n$-type material and of the levels $H_4$ and $EP_2$ in the $p$-type material, as a function of the incoming electron energy. The data for $H_4$ and $E_{11}$ include ours and those of Ref. 2. The dashed line corresponds to the $H_4$ level and is extracted from Ref. 2.

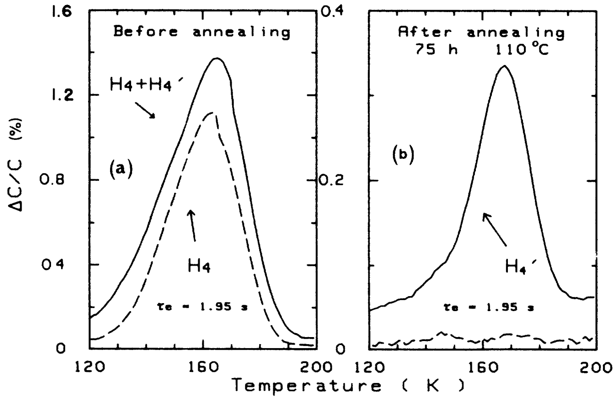

FIG. 3. (a) Amplitude variation and temperature shift of the DLTS peak attributed to $H_4$ when the filling pulse duration is changed from 0.5 ms to 4 s (solid line). (b) After subsequent annealing the contribution of $H_4$, dashed line, has vanished and $H_4'$ is totally resolved.

### B. Annealing of $H_4$ and $E_{11}$

The hole level $H'_4$ is generated by secondary reactions of the EIID's since it is not detected in unirradiated samples giving the same thermal treatment. Additionally, the thermal generation of $H'_4$ is only observed in the Zn-doped Schottky or $n^+$-$p$ junctions, but not in the Cd Schottky junctions.

Since it has been previously established that the annealing kinetics of $H_4$ are exactly first order in Cd-doped InP, but not in Zn-doped InP, this sensitivity of the generation of $H'_4$ to the acceptor species is a good indication that the increase of $[H'_4]$ is related to the disappearance of $H_4$.

The strong correlation between the thermal generation of $H'_4$ and the annealing out of $(H_4$-$E_{11})$ is clearly demonstrated by the simultaneous study of their concentration changes in the same sample. To do so, the annealing procedure was accelerated by a minority-carrier injection, i.e., electron injection in the $n^+$-$p$ junctions used. The relative contributions of $H_4$ and $H'_4$ to the DLTS spectra are easily separated by changing the filling pulse duration, and the changes in the respective concentrations of $H'_4$, $H_4$, and $E_{11}$ were also measured by thermostimulated-capacitance scans.

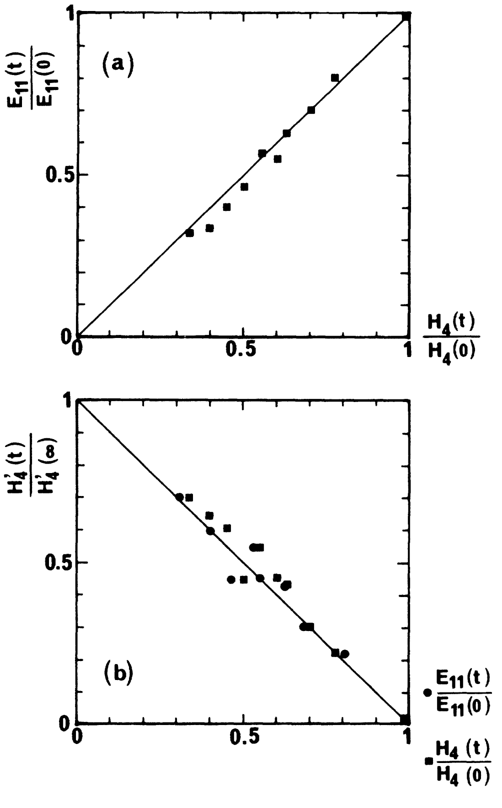

FIG. 4. (a) Comparison, during annealing, of the concentrations of the levels $E_{11}$ (ODLTS) and $H_4$ (DLTS). Both concentrations are normalized to their initial value. (b) Comparison, during annealing, of the normalized concentrations of the vanishing levels $H_4$ or $E_{11}$ and of that of the growing defect $H'_4$. In these experiments, the annealing process is enhanced by electron injection under saturated conditions, $J=6$ A cm$^{-2}$. The final efficiency of the defect transformation $(H_4$-$E_{11})\rightarrow H'_4$ is 0.2 to $\sim$0.3.

The results are collected together in Fig. 4. They show, that in Zn-doped InP the following is true.

The annealing kinetics of $H_4$ and $E_{11}$ are identical.

The annealing of the hole level $H_4$ and also of the electron trap $E_{11}$ are enhanced in the same way by the electron injection and occur below RT.

The growth kinetics of $H'_4$ reflects exactly the joint disappearance of $(H_4$-$E_{11})$.

The defect transformation $(H_4$-$E_{11})\rightarrow H'_4$ is an 0.2 to 0.3 transformation (see Fig. 5), but an exact balance is difficult since in the case of $H_4$ and $H'_4$ the DLTS peak amplitude depends on the level depth and because optical filling is used for $E_{11}$.

Even though the recombination-enhanced annealing kinetics of $(H_4$-$E_{11})$ is not first order, we have measured the temperature dependence of the initial slope,

$$K_{(T)}=-\frac{1}{[H_4]}\frac{d[H_4]}{dt}=-\frac{1}{[E_{11}]}\frac{d[E_{11}]}{dt} ,$$

and found that it is well described by

$$K=3.3\times 10^3 \exp\left[-\frac{0.22\text{ eV}}{kT}\right] .$$

Comparison of this result with previously published data is made in Table I. These agree, within the experimental uncertainties, with the results of Refs. 3, 5, and 14 on the hole trap $H_4$.

In the case of Cd doping (Schottky diodes and thermal treatment) the hole trap $H_4$ and the minority-carrier trap $E_{11}$ are still observed to have exact first-order annealing kinetics, in perfect agreement with Ref. 3, but the generation of $H'_4$ is no longer observed.

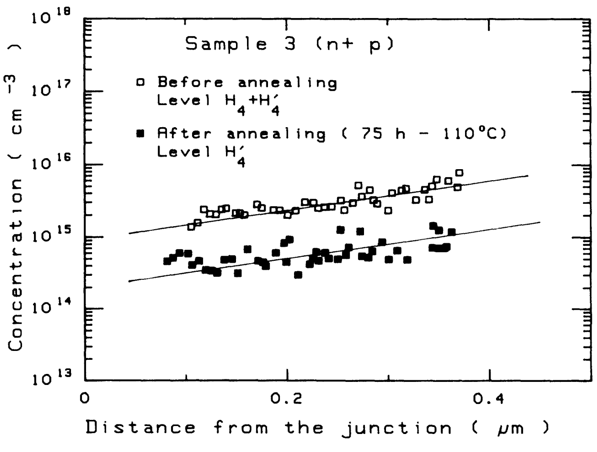

FIG. 5. Defect concentration profiles, obtained by differential deep-level transient spectroscopy, of the initial EIID $H_4$ before annealing, and of the generated level $H'_4$.

TABLE I. Values of the activation energy, $E$, and of the pre-exponential factor, $\nu$, of the annealing rates: $K=\nu\exp(-E/kT)$, of the electron-irradiation-induced defects $H_4$ and $E_{11}$. When the process is not first order, under minority-carriers injection, for instance, the values are taken at the beginning of the annealing.

| Level $H_4$ | | Empty of holes | Filled with holes | With additional electron injection | Refs. |
|---|---|---|---|---|---|
| $p$-type InP | $E$ (eV) | 1.32 | 1.69 | 0.24 | 3,5,14 |
| | $\nu$ ($s^{-1}$) | $2\times10^{15}$ | $2\times10^{18}$ | $2.8\times10^{4}$ | |
| | $E$ (eV) | | 1.02 | 0.133 | 7,8 |
| | $\nu$ ($s^{-1}$) | | $2.72(p)^{2/3}$ | $19.35J$ | |
| | $E$ (eV) | | 1.69 | 0.22 | |
| | $\nu$ ($s^{-1}$) | | $2\times10^{18}$ | $3.3\times10^{3}$ | this work |
| $n$-type InP | $E$ (eV) | 0.68 | | | 7 |
| | $\nu$ ($s^{-1}$) | $1.5\times10^{15}$ | | | |
| Level $E_{11}$ | | Empty of electrons | Filled with electrons | With additional hole injection | Refs. |
| $n$-type InP | $E$ (eV) | 1.32 | 1.27 | | 3,5,14 |
| | $\nu$ ($s^{-1}$) | $2\times10^{15}$ | $3\times10^{15}$ | | |
| | $E$ (eV) | 1.30 | 1.30 | 0.42 | 12 |
| | $\nu$ ($s^{-1}$) | $1\times10^{15}$ | $2\times10^{16}$ | $10^{3}$ | |
| | | | | With additional electron injection | |
| $p$-type InP | $E$ (eV) | | | 0.22 | |
| | $\nu$ ($s^{-1}$) | | | $3.3\times10^{3}$ | this work |

## V. PHYSICAL PROPERTIES OF THE HOLE TRAP $H_4'$

The hole emission rates of $H_4$ and $H_4'$ are shown for comparison in Fig. 6. Their hole emission times differ by a factor of about 2 to 5. Least-squares analysis of these data gives rather different signatures:

| | $E_a$ (eV) | $\sigma_a$ ($cm^2$) |
|---|---|---|
| $H_4$ | 0.37 | $8\times10^{-16}$ |
| $H_4'$ | 0.50 | $4\times10^{-12}$ |

The drastic difference between $H_4$ and $H_4'$ lies in their hole-capture properties. Actually, we could not proceed to direct measurements of the hole-capture cross section of $H_4$ since its capturing time $\tau_c=(p\sigma v)^{-1}$, estimated from $p\sim10^{16}$ cm$^{-3}$, $v\sim10^{7}$ cm s$^{-1}$, and $\sigma\sim10^{-15}$ cm$^{2}$, is in the 10-ns range. By contrast the filling efficiency measurements of $H_4'$ are made difficult by its very long filling time $\tau_c$ which is in the ms range at 190 K but increases exponentially to more than 100 s near 120 K. The hole emission time $\tau_e$, being greater than 10 s at $T<160$ K optical emptying, was used below this limit to increase the temperature range to 110 K.

Data for the hole-capture cross section of $H_4'$ are shown in Fig. 7. It is thermally activated and well described by

$$\sigma_{(T)}(\text{cm}^2)=10^{-13}\exp\left[-\frac{0.27\ \text{eV}}{kT}\right],$$

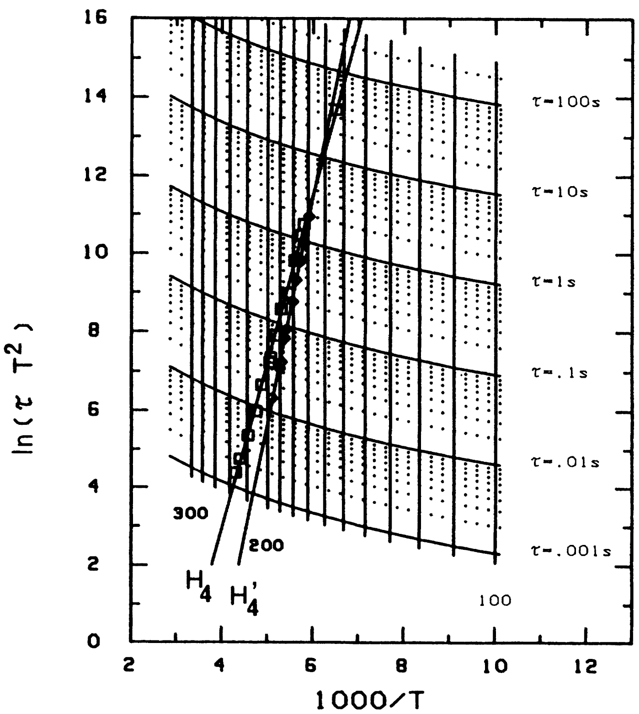

FIG. 6. Direct comparison of the hole emission rates of $H_4$ ($E_a=0.37$ eV, $\sigma_a=8\times10^{-16}$ cm$^{-2}$) and of $H_4'$ ($E_a=0.50$ eV, $\sigma_a=4\times10^{-12}$ cm$^{-2}$). Constant values of the emission time $\tau$ are shown to allow an easier comparison with other results.

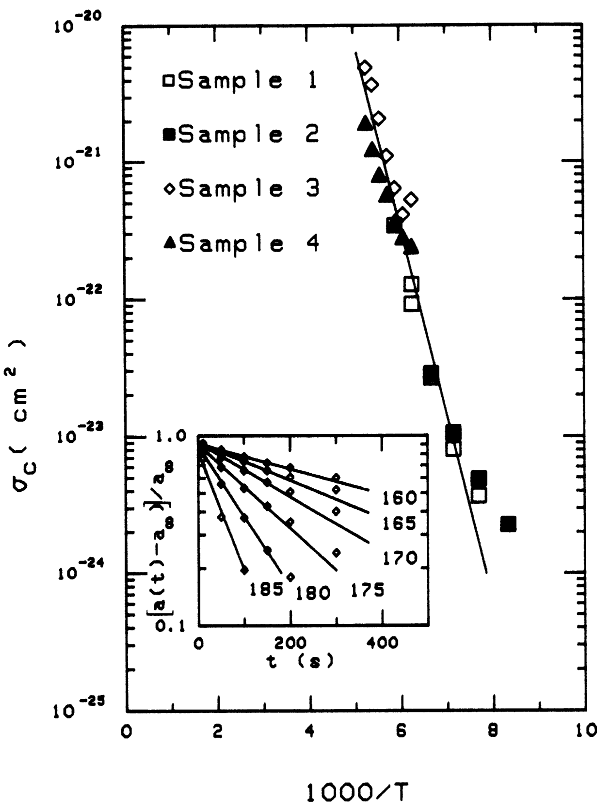

FIG. 7. Direct measurements of the hole-capture cross section of $H_4'$ in various samples. Samples 1 and 2, Schottky diodes on $p$ type with $p \approx 3\times10^{16}$ cm$^{-3}$; samples 2 and 3, $p^+$-$p$-$n^+$ diodes with $p\approx 6\times10^{16}$ cm$^{-3}$. Below 160 K optical emptying is used in place of thermal emptying. The capturing time $\tau_c$ is larger than 100 s at 120 K. The inset shows that the hole filling is perfectly exponential $a(t)=a_\infty[1-\exp(-t/\tau_c)]$.

as expected in a multiphonon-emission process (MPE) when $kT > \hbar\omega$. Such a MPE process implies a saturation of $\sigma_c$ at low temperatures, when $kT < \hbar\omega$, which was not actually observed. The $T\rightarrow\infty$ extrapolated value of $\sigma_c$, $10^{-13}$ cm$^2$, is comparable to that obtained from DLTS, $\sigma_a=4\times10^{-12}$ cm$^2$, indicating a small entropy change during the hole trapping.

The optically induced valence-band (VB)$\rightarrow H_4'$ electron transition was observed and the spectral dependence of the corresponding photoionization cross section $\sigma_p^o$ was measured and analyzed with the help of a previously described experimental setup and fitting procedure.[16] The results are shown in Fig 8.

The experimental onset is at $h\nu=0.6$ eV; the solid curve corresponds to the least-squares fit to an analytical expression of the type used by Chantre, Vincent, and Bois[17] with the usual approximations of an equivalent parabolic band, a constant dipole matrix element, and an assumed $1/r\exp(-\alpha r)$ isotropic bound state.

As in the case of the initial EIID $H_4$, the complementary $H_4'\rightarrow$conduction-band (CB) transition could not be optically induced and all our attempts with various wave-

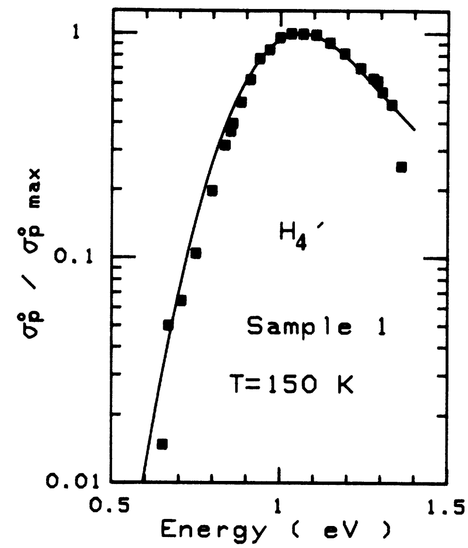

FIG. 8. Spectral dependence of the normalized photoionization cross section $\sigma_p^o$ of $H_4'$. The solid line corresponds to the analytical expression of Ref. 17 with an optical threshold $E_p^o=0.95\pm0.2$ eV and an assumed $(1/r)\exp(-\alpha r)$ bonded state with $\alpha^{-1}=0.25$ Å.

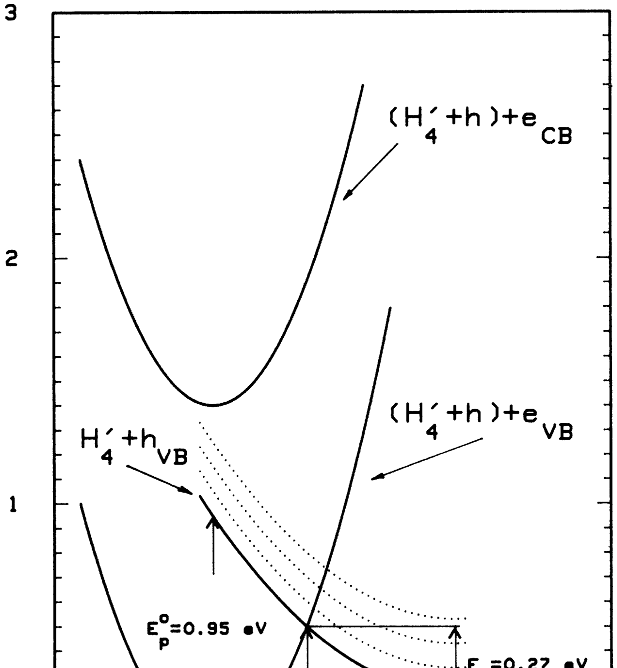

FIG. 9. Configuration-coordinate diagram of $H_4'$ which accounts for the weak values and the thermal activation of its hole-capture cross section. The curvature of the infinite set of parabolas in the free-hole state has been slightly reduced to adjust the optical threshold to 0.95±0.2 eV. The optical transition of the bonded electron in the $H_4'+h_{VB}$ state to the conduction band requires $h\nu > Eg$.

length and illumination conditions were unsuccessful.

These very weak cross sections and the thermal activation of the hole-capture cross section of $H'_4$, as well as the impossibility of inducing the $H'_4 \rightarrow$CB electron transition by optical excitation, are well explained in a phenomenological way with the help of the one-dimensional configuration-coordinate diagram (CCD) shown in Fig. 9 which displays the very large lattice relaxation following the hole delocalization.

However, the values of $E_a = 0.50$ eV and $E_b = 0.27$ eV corresponding to an equilibrium depth $E_t = 0.23$ eV cannot be exactly reconciled with $E_p^0 \sim 0.95 \pm 0.2$ eV. Consequently, the curvature of the infinite set of parabolas in the free-hole state has been slightly reduced without altering the qualitative validity of the model.

## VI. DISCUSSION

As discussed in Sec. I, the common character of the RT annealing of the hole trap $H_4$ and the electron trap $E_{11}$ was first outlined by Sibille,[3] who observed that in a pure thermal process the effective frequency,

$$K = 2 \times 10^{15} \exp\left[-\frac{1.32\ \text{eV}}{kT}\right],$$

is exactly the same in their respective hole and electron-free states when measured, respectively, in $p$- and $n$-type InP.

The high prefactor of the transformation indicates that the moving atomic entity undergoes only one or a few atomic jumps, and the common activation energy (1.3 eV) of the atom that moves is probably the same.

The experiments described in Sec. IV bear out the common annealing of $H_4$ and $E_{11}$ during a pure thermal process in Zn- and Cd-doped crystals and also under electron injection in the Zn case. This demonstrates that the energy released in the electron-hole recombination enhances exactly in the same manner the annealing of both these two levels. Furthermore, the sensitivity of the annealing kinetics of $H_4$ to the doping species, Zn or Cd, is confirmed by the present experiments, is also demonstrated for $E_{11}$, and is clearly related to the occurrence of the quasi-one-for-one transformation $(H_4, E_{11}) \rightarrow H'_4$. These common properties of the $[D(\text{P})\text{-}A^-]$ complex at the origin of the electronic levels $H_4$ and $E_{11}$ can be clearly understood in the following three possible cases.

(a) $H_4$ and $E_{11}$ correspond to two different and separated complexes which react together in a one-for-one ratio, to generate $H'_4$.

(b) $H_4$ and $E_{11}$ correspond to two different but related complexes and their annealings are governed by the same local jump of their common atomic entity.

(c) $H_4$ and $E_{11}$ correspond to two different charge states of the same $[D(\text{P})\text{-}A^-]$ complex.

The hypothesis (a) $H_4 + E_{11} \rightarrow H'_4$, which implies a second-order creation rate, is rejected since the initial concentrations of $H_4$ and $E_{11}$, $10^{14}$ to $10^{15}$ cm$^{-3}$, are much too low to explain the nearly 0.2 efficiency of the reaction, since it implies a long-range migration and a reassociation of randomly distributed defects.

The hypothesis (b), with $H_4$ and $E_{11}$ corresponding to two related $[D(\text{P})\text{-}A^-]$ complexes, implies that the moving common entity is $D$(P) since the acceptor is more than likely stable in the In-substituted site. In this hypothesis $H_4$ and $E_{11}$ can hardly be viewed as corresponding to two different distant $[D(\text{P})\text{-}A^-]$ pairs, first and second neighbor for instance, since their concentrations are approximately equal, and, on the other hand, $H_4$ and $E_{11}$ can scarcely correspond to two different sites of the phosphorus sublattice defect $D$(P) since the identity of their annealing kinetics is strictly maintained under electron injection which generates local modes of vibration with an efficiency which depends critically on the local symmetry.

For these reasons we propose to explain the full identity of their annealing kinetics by assuming, hypothesis (c), that $H_4$ and $E_{11}$ correspond to two different charge states of the same $[D(\text{P})\text{-acceptor}]$ complex. Assigning to this complex a zero net charge without bonded electrons we propose that $H_4$, at $E_v + 0.37$ eV, corresponds to the energy change $E^{-/0}$ needed for the first ionization,

$$C^0 + e_{\text{VB}} \rightarrow C^-,$$

and that $E_{11}$, at $E_g - 0.72 = E_v + 0.65$ eV, corresponds to the second ionization step,

$$C^- + e_{\text{VB}} \rightarrow C^{2-}.$$

With such a simple hypothesis the complex $C$ is in the charge state $C^-$ in much of an $n^+$-$p$ junction and in the charge state $C^{2-}$ in a $p^+$-$n$ junction.

In the $n^+$-$p$ junction the $C^- \rightarrow C^0$ transition, level $H_4$, is induced by the hole accumulation under forward bias and is then followed by the hole re-emission to the VB (DLTS). The $C^- \rightarrow C^{2-}$ transition, level $E_{11}$, can be induced by optical excitation from the VB and is followed by the thermal re-emission of the seond trapped electron to the CB (DLOS). In a reverse-biased $p^+$-$n$ junction and at sufficiently high temperatures the $C^- \rightarrow C^{2-}$ transition is induced by forward biasing and the level $E_{11}$ is observed by DLTS, while the $C^- \rightarrow C^0$ transition, corresponding to the level $H_4$, is difficult to observe by ODLTS since we have verified on $p$-type material that the required electron transition from $H_4$ to the conduction band cannot be optically induced with a high enough efficiency to overcome the simultaneous VB$\rightarrow H_4$ optical transition. It is true, however, that Yamaguchi and Ando (Ref. 10 and references therein) have observed hole traps in the $n$-type material by ODLTS, with activation energies close to that of $H_4$, but the identification of one of them with $H_4$ is questionable, and the exact balance between the optical emptying frequency $\sigma_p^o \phi$ and the total refilling frequency $\sigma_p^o \phi + nSv$ is not the same in a $p^+$-$n$ junction and in a $n^+$-$p$ one with the $[D(\text{P})\text{-}A^-]$ complex located in both cases near the $p$ side.

To go one step further, without being unduly speculative, we propose that the initial phosphorus irradiation damage $D$(P) of the $[D(\text{P})\text{-}A^-]$ complex is the phosphorus vacancy $V_\text{P}$ and that the observed levels $(H_4, H'_4)$ and $E_{11}$ correspond essentially to its $a_1$ and $t_2$ levels more or less perturbed by the local reduction of symmetry due to the acceptor pairing or to static Jahn-Teller distortions.

Our first reason is that the position in energy in the forbidden gap of $H_4$, $H'_4$, and to a lesser extent of $(H_2,H_3)$, coincides, with an accuracy better than 0.2 eV, with the $a_1$ level of the unrelaxed phosphorus vacancy calculated in the second-neighbor tight-binding framework by Talwar and Ting[18] for the neutral $V^0$ state and by Delerue and Lannoo[19] for the three charge states, $V^0$, $V^+$, and $V^{2+}$ (see Table II). From these it is more than likely that the mobile free vacancies $V_P$, generated by the electron collision, are positively charged and associate under electrostatic attraction with the ionized acceptors.

The second reason is that these phosphorus vacancies have actually been observed at RT by von Bardeleben using electron paramagnetic resonance[20] (EPR) after 1.5-MeV irradiation of Zn-doped InP. The observed $S=\frac{1}{2}$ EPR spectrum was attributed to $V^0$, with three bonded electrons, but it can just as well be attributed to $V^{2+}$ with a single electron. This EPR active defect has an introduction rate, 1 $\text{cm}^{-1}$, comparable to those of $H_4$ and $E_{11}$. However, a complete identification with $H_4$ was rejected since it begins to anneal at RT in the highly doped samples ($p > 1.10^{17}\ \text{cm}^{-3}$).

The third reason is that the photoionization cross-section measurements of $H_4$ and $E_{11}$ have shown that $H_4$ behaves essentially as an $a_1$ state of the $T_d$ host crystal, with only one allowed $(\Gamma_8+\Gamma_7\rightarrow a_1)$ transition, while $E_{11}$ behaves essentially as a $t_2$ state with both the VB$\rightarrow E_{11}$ and $E_{11}\rightarrow$CB allowed transitions. Of course the local symmetry of a $(V_P\text{-}A^-)$ pair is reduced at least to $C_{3v}$ by the pair axis, and probably furthermore by local distortions, but the general frame is still valid and the only difference expected is that the $a_1\rightarrow$CB dipole transition is not strictly forbidden. In this scheme, $E_{11}$, with its trapped electron on the $t_2$ level, would correspond to the perturbated $V_P^0$ state, and the electron release by $E_{11}$ would correspond to the $(V_P^0\text{-}A^-)\rightarrow(V_P^+\text{-}A^-)$ transformation. In the same context $H_4$ would correspond to the $(V_P^{2+}\text{-}A^-)\rightarrow(V_P^+\text{-}A^-)$ transition with the trapping of an electron on the $a_1$ state. The 0.5-eV difference between $E_{11}$, at $E_v+0.65$ eV, and the calculated values of the $V_P^+$ $t_2$ levels at $E_v+1.2$ eV, can be explained by the splitting of the $t_2$ levels during the local reduction of symmetry in the $A^-$ pairing.

TABLE II. Calculated positions of the localized states due to the unrelaxed and isotropically charged phosphorus vacancy, $V_P$, in InP. The origin of the energies is taken at $E_v$.

| | | $a_1$ level | $t_2$ level |
|---|---|---|---|
| Ref. | Charge state | $(E-E_v$ in eV) | |
| 18 | $V^0$ | 0.28 | 1.5 |
| 19 | $V^0$ | 0.54 | 1.32 |
| | $V^+$ | 0.38 | 1.2 |
| | $V^{2+}$ | 0.19 | 1.0 |

With such a simple hypothesis one can explain the following in a natural way.

The identity of the annealing kinetics of the $H_4$ and $E_{11}$ levels in their respective hole and electron-free states identified to $(V_P^+\text{-}A^-)$.

The slower annealing of $H_4$ in its hole-filled state and the faster annealing of $E_{11}$ in its electron-filled state by the increase and decrease of the electrostatic attraction in the $(V_P^{n+}\text{-}A^-)$ pair.

The markedly less efficient generation of the EIID defects in the $n$-type InP than in the $p$-type InP and the necessity to use $p^+$-$n$ junctions and not Schottky barriers to observe $E_{11}$. In the $p$-type material the $V_P^{2+}$ or $V_P^{3+}$ free vacancies associate with the negatively charged ionized acceptors to form complexes, while, in the $n$-type material, the free-phosphorus vacancy $V_P$, with its $t_2$ levels close to the conduction band, acts essentially as a donor. This donor character of the free-phosphorus vacancy also explains the unusual increase of the capacitance of $p^+$-$n$ junctions subjected to very high irradiation doses, $>2\times10^{16}$ $e\ \text{cm}^{-2}$, instead of the usual decrease, since in this case $[V_P]$ becomes comparable or larger than the acceptor concentration in the doping tail of the $p^+$-$n$ junction.

Anyway, even if we concede that the proposed $(V_P\text{-}A^-)$ pair complex needs to be supported by microscopic observations, such as by EPR experiments, one must try to explain the different annealing behavior of $(H_4\text{-}E_{11})$ in Cd- and Zn-doped $p$-type InP which is shown in Sec. IV to be clearly related to the concomitant generation of $H'_4$. The key observations are the following.

In a pure thermal treatment the process is exactly first order with Cd and does not generate $H'_4$, while it is approximately first order with Zn and generates $H'_4$ with a weak efficiency.

Under saturated electron-injection conditions and Zn doping the annealing is no longer first order and the defect transformation $(H_4\text{-}E_{11})\rightarrow H'_4$ has approximately a one-for-one efficiency.

Clearly this is the defect transformation $(H_4\text{-}E_{11})\rightarrow H'_4$ which is the most efficiently enhanced by the free-carrier recombination and which is responsible for the observed changes in the annealing kinetics. This selective enhancement can be understood by the preferential generation of specific phonon modes during the free-carrier recombination and has also been observed for the stage-I $(H_2\rightarrow H_4)$ defect transformation.[14] For instance, one can assume that the dissociation of the $(V_P\text{-Zn}^-)$ complex can be achieved by at least two different paths for the moving atomic entity, with two different dominant local phonon modes, and that the one leading to $H'_4$ is more efficiently excited by the free-carrier recombination. The same hypothesis can also account for the sensitivity of the annealing kinetics to the acceptor species, Cd or Zn, since the dominant phonon mode of the $(V_P\text{-}A^-)$ pair depends on the atomic masses and on the bond strengths.

To be more quantitative one can, for instance, assume that in the case of Cd or Zn together with a thermal-phonon distribution the complex $C=(V_P\text{-}A^-)$ undergoes dissociation and that the released vacancies are either recaptured or annihilated to sinks after rapid diffusion, leading to the following reaction scheme:

$$\begin{tikzcd} C \arrow[r, shift left, "K_{\text{diss}}"] & A^- + V \arrow[l, shift left, "K_C"] \arrow[d, "K_{\text{an}}"] \\ & \text{sinks} \end{tikzcd}$$

while in the case of Zn and electron injection, the REDR mechanism, this dissociation runs concurrently with the transformation leading to $H'_4$. In the first case the solution of the two coupled equations,

$$\frac{d[C]}{dt} = -K_{\text{diss}}[C] + K_c[A^-][V]$$

and

$$\frac{d[V]}{dt} = -K_{\text{an}}[V] - K_c[A^-][V] + K_{\text{diss}}[C] \;,$$

is straightforward using Laplace transforms. As long as recapture is negligible, i.e., as long as $K_c[A^-] < K_{\text{an}} + K_{\text{diss}}$, the kinetics are exactly first order with $K_{\text{eff}} = K_{\text{diss}}$. However, the exact solution depends critically on the ratio $K_c/(K_{\text{an}} - K_{\text{diss}})$, and for low values of this ratio it is well approximated by

$$C(t) \approx C_0 \left[ 1 + \frac{K_c}{K_{\text{an}} - K_d} \right] e^{-K_d t} - C_0 \frac{K_c}{K_{\text{an}} - K_d} e^{-K_{\text{an}} t} \;.$$

This contribution of two exponential terms can explain the weak difference of the observed pure thermal annealing kinetics of ($H_4$-$E_{11}$) in Zn- and Cd-doped samples since the recapture of the released vacancies is probably higher with Zn than with Cd.

Under electron injection the dissociation of [$C$] runs concurrently with the transformation into $H'_4$ characterized by an effective frequency $K_t$, and $K_{\text{diss}}$ is simply replaced by $K_d = K_{\text{diss}} + K_t$. The resulting kinetics are still the sum of two exponential processes, but in this case they may be of comparable magnitude if the recombination modified constants $K'_c$, $K'_{\text{an}}$, and $K'_d$ are such that $K'_c$ is comparable to $K'_{\text{an}} - K'_d$.

## VII. CONCLUSION

The study of the simultaneous annealing out of the two dominant electron-induced-irradiated defects in InP, the hole trap $H_4$ at $E_v + 0.37$ eV and the electron trap $E_{11}$ at $E_c - 0.72$ eV, made in Cd- or Zn-doped $n^+$-$p$ junctions, confirms that they are correlated and strongly supports the idea that they result from the same microscopic defect.

In the case of Zn doping the annealing out of ($H_4$-$E_{11}$) generates another localized level $H'_4$ with a thermally activated hole-capture cross section in the $10^{-24}$-cm$^2$ range which makes it undetectable in usual deep-level transient spectroscopy experiments.

This hole trap $H'_4$ is generated by a local-defect transformation, with an approximate 5% efficiency in a pure thermal treatment, and a 0.3 efficiency with additional free-carrier recombination. This local-defect transformation ($H_4$-$E_{11}$)$\rightarrow H'_4$ is responsible for the observed differences of the annealing kinetics in Cd- and Zn-doped samples.

The optical properties of $E_{11}$ and $H_4$ are drastically different since in the case of $E_{11}$ both electronic transitions from the valence band to $E_{11}$ or from $E_{11}$ to the conduction band are optically induced, while in the case of $H_4$ the transition to the CB could not be observed.

The full identity of the annealing properties of $H_4$ and $E_{11}$ under varied conditions is interpreted by assuming that they correspond to two different charge states of the same $V$(P)-$A^-$ complex. This explains in a natural way the difference in their optical properties and the known low introduction rates of EIID's in $n$-type InP where the unpaired phosphorus vacancies $V$(P) act essentially as shallow donors.

The local character of the dominant mechanism of the thermal annealing is also demonstrated for the defect transformation ($H_4$-$E_{11}$)$\rightarrow H'_4$, and the sensitivity of the exact kinetics to the doping species, as well as to the physical treatment, is assigned to the modified balance between the rate of dissociation of the $V$(P)-$A^-$ complex and the rate of recapture of the released vacancy.

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