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Metastable Electron-Hole-Pair Self-Trapping at a Deep Center in InP

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Strong evidence is given of electron-hole-pair trapping at a deep center in InP. The observation of this new kind of metastable state, which had been theoretically predicted, is made possible because of the small value of the recombination rate between the two carriers in a wide temperature range. A model in terms of configuration coordinate diagram is proposed to account for this unusual behavior.

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The electron-phonon interaction has taken various aspects in semiconductors. In particular, its occurrence for point defects has been demonstrated in many materials[1]; coupling between trapped carriers and lattice deformation may be weak (as for shallow impurities) or strong (as exhibited by some deep centers). The latter situation, leading sometimes to peculiar effects, has long been investigated in ionic crystals, and more recently, actively studied in covalent semiconductors.[1-4] Yet, in all cases reported so far, only one type of carrier was involved for single or multiple trapping at a given center.

This Letter describes experimental work showing for the first time that a defect in InP can successively bind a hole and an electron which do not instantaneously recombine, and thermally reemit them. This behavior, in disagreement with Schockley-Read kinetics,[5] is suspected to be caused by a new manifestation of electron-phonon interaction. We applied transient capacitance and current methods including deep-level transient spectroscopy (DLTS)[6] to p^+n diodes prepared by Zn diffusion into undoped n-type InP melt-grown crystals ($n \simeq 10^{15}$ cm^{-3}). A deep center located in the space-charge zone of the semiconductor can be detected by thermal emission of trapped electrons or holes previously captured during a bias pulse. The capacitance or current transients associated with this emission were analyzed either by a double-phase lock-in amplifier for DLTS experiments, or by a computer.

Three DLTS spectra are presented in Fig. 1, together with the corresponding pulse sequences. Curve *a* exhibits two negative peaks $E1$ and $E2$ indicating majority carrier (electron) emission, a usual behavior since the bias remained reverse. $E2$ closely resembles the peak designated as E in Wada *et al.*[7] Curve *b* was recorded by using the previous voltage sequence with an additional 10-mA, 100-μs forward-current pulse. Quite unexpectedly, the main change caused by the latter is the appearance of a new peak, labeled ES. The relevant electron emission can only be

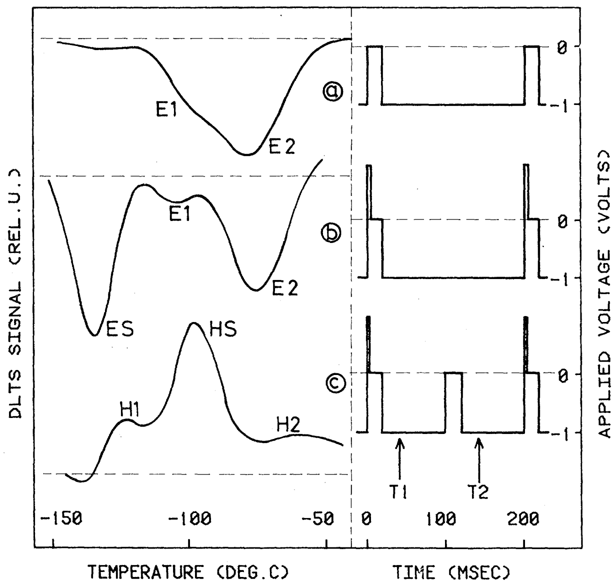

FIG. 1. Left-hand side, DLTS spectra corresponding to the pulse sequences presented on the right-hand side. Dashed lines are zero level. Data acquisition times $T1$, $T2$ are 40 and 140 msec, dc bias is -1 V. Curve *a*, +1 V, 20 msec pulse; curve *b*, same as *a* plus a 10-mA, 100-μs forward pulse; curve *c*, same as *b* with an additional +1-V, 20-msec pulse 100 msec delayed.

observed after hole injection. If the pulse sequence is abruptly changed from b to a, peak ES does not immediately disappear, but decays slowly. Moreover, a white-light continuous illumination of the sample (inducing a measurable photocurrent) together with pulse sequence a also leads to the observation of peak ES. The very same slow decay behavior is found when light is removed. All of these experiments prove without ambiguity that ES cannot be seen unless minority carriers crossed the junction.

In order to clarify this, we measured the decay rate τ_E^{-1} of peak ES after the application of a single-hole injecting pulse, followed by a sequence of electron refilling pulses. It was found that τ_E^{-1} increased with the pulse frequency F (Fig. 2). Clearly this means that peak ES decays faster if the center, S, is more often filled with the electron.

All of these experimental observations can be explained in the following way: At each refilling pulse, an electron can be trapped on the center S only if it is already filled with a hole (captured during the initial forward pulse). No immediate recombination takes place and both carriers are individually trapped. The slow decay is due to a gradual disappearance of holes, partly by thermal emission, partly by slow recombination between the two trapped carriers. Indeed, the slow decrease of the capacitance signal before each pulse associated with this disappearance was actually observed with the same rate and amplitude (Fig. 2). The dependence of τ_E^{-1} on F clearly points out that the recombination contribution is not negligible.

A simple calculation can quantitatively give an account of this model: Let E_n be the emission rate of the electron, E_h that of the hole once the electron is free, R the recombination rate per unit time and S center, $N(t)$ the number of centers occupied by a hole or a pair, and $N(t)f(t)$ the number of centers occupied by a pair $(0<f<1)$. Then,

$$dN = -N(t)[Rf + E_h(1-f)]\,dt \tag{1}$$

approximately describes the slow processes, i.e., hole emission and pair recombination. Holes are injected at $t=0$: $f(t)$ is a function of period $1/F$; $f(t)=\exp(-E_n t)$ if $0<t<1/F$.

The integration is easy if $t=\text{integer}/F$:

$$\ln N(t)/N(0) = -E_h t - [(R-E_h)/E_n][1-\exp(-E_n/F)]Ft; \tag{2}$$

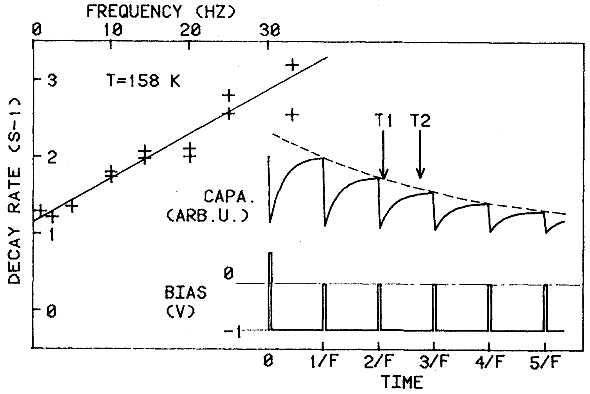

FIG. 2. Decay rate τ_E^{-1} of peak ES vs frequency F, using the voltage sequence shown on the right-hand side. The first pulse is a 100-μs, 10-mA hole-injecting pulse. For each frequency, the decaying quantity is either $C(T1)-C(T2)$ (amplitude of transient ES) or $C(T2)$ (dashed line), where C is the capacitance signal. Crosses are the experimental decay rates. The full line is theoretical fit using Eq. (3).

for $E_n \gg F$, which was true in our measurements, we find an effective decay rate

$$\tau_E^{-1} = E_h + [(R-E_h)/E_n]F. \tag{3}$$

τ_E^{-1} is plotted versus frequency in Fig. 2. The straight line predicted by Eq. (3) fits the experimental points reasonably well. At $F=0$, we find a nonzero intercept proving that hole emission is not negligible.

To make this more obvious, a DLTS scan was recorded with pulse sequences and acquisition times $T1$ and $T2$ of Fig. 1, curve c. All majority carrier emissions are subtracted because of the 20-msec regenerating pulse at $1/2F$. Three positive peaks $H1$, $H2$, and HS, masked by the negative part of the spectrum in Fig. 1, curve b, are beautifully extracted. In particular, the amplitude of HS is very close to that of ES and its signature correlates perfectly with E_h, determined with Fig. 2. Also using transient current measurements, we found a 0.25-eV activation energy for ES and 0.36 eV for HS over four decades. At 158 K, we have only $R=30\ \text{s}^{-1}$, whereas $E_n \simeq 580\ \text{s}^{-1}$. By varying the reverse bias and pulse height, a concentration profile of S centers was estimated, which showed no strong singularity and an average value of trap density $N_T \simeq 10^{14}\ \text{cm}^{-3}$; ES could be observed in the range 110–200 K.

Let us now try to understand this metastable effect. Strong lattice relaxation, which is often predominant in many respects for deep levels,

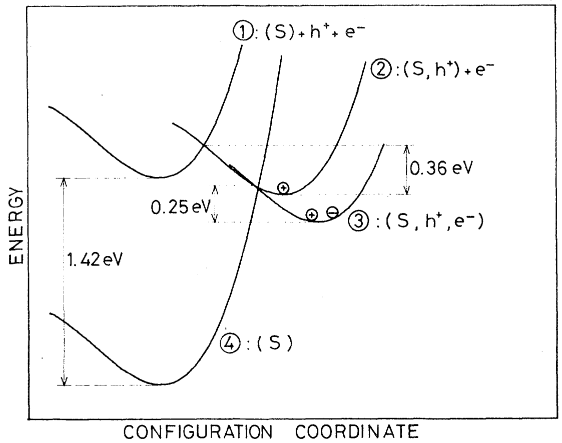

FIG. 3. Configuration coordinate diagram for the different states of defect *S*. A carrier is free if outside, trapped if inside the brackets.

must be suspected here. Concerning multicarrier trapping, it was very recently invoked to account for the negative *U* behavior of the vacancy in Si.[4] On the other hand, exciton self-trapping has long been known to exist in ionic crystals, with several possible situations: In the first, both carriers are tightly bound with the help of the lattice[7]; in the second, one is deeply trapped and the other is bound by the Coulomb field.[8] Sumi[9] theoretically studied in detail the general case of electron-hole pair coupling with the lattice. He found the previous situations, respectively called (III^+) and (II), and also a new one (III^-) where both carriers can be individually self-trapped. His calculation concerned a perfect lattice, but interaction with the vibration modes of a defect might also induce (III^-). We think our experiments demonstrate this possibility. It must also be mentioned that a similar case seems to have been found in amorphous semiconductors.[10]

To go further, we propose the configurational coordinate diagram of Fig. 3. Energies are positively counted up. Each curve gives the energy of the system defect electron hole in different states versus an internal coordinate of defect *S*. For the metastable state (S, h^+, e^-) to be reached, we have (i) trapping of a hole $(1 \rightarrow 2)$, (ii) capture of an electron $(2 \rightarrow 3)$. Two paths are then possible: (iii) thermal emission of the electron $(3 \rightarrow 2)$, or (iv) temperature-activated recombination $(3 \rightarrow 4)$.

This scheme is reasonable if all three curves 2, 3, and 4 cross at very close points so that (iii) and (iv) could effectively compete. However, the one-dimensional representation suggested here is probably a very rough one.

In summary, we have observed for the first time in a crystalline nonionic semiconductor the metastable trapping of an electron-hole pair at a defect and proved that low temperatures were not necessary. The phenomenological model of configuration coordinates was tentatively adapted and it was shown that the observed properties could be explained by a strong coupling with the lattice. Work is in progress to get more information on the nature of this defect. We wish to thank P. Devoldere for help in sample preparation and D. Paquet and K. Rao for fruitful discussions.

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