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Nonradiative-recombination-enhanced defect-structure transformation in low-temperature γ-ray-irradiated InP

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Low-temperature γ-ray irradiation and subsequent minority-carrier injection are found to enhance a defect-structure transformation from a major irradiation-induced deep hole trap ($E_v+0.32$ eV) to a deeper hole-trap center ($E_v+0.52$ eV) in p-type InP. Direct experimental evidence is shown to demonstrate the role of the 0.32-eV level as an efficient nonradiative recombination center which competes with other radiative transition channels. The results show a recombination-enhanced reaction mechanism at the anion-displacement center with strong electron-phonon couplings.

Defect reactions in semiconductors exhibit unique properties, in that a variety of electronic effects can affect the defect reaction kinetics of a simple thermally activated process. Detailed understanding of these phenomena is important not only in practical device degradation (or recovery) mechanisms[1,2] but for finding new reaction processes involving various defect–electronic-system interactions.

This Communication presents the first observations of a minority-carrier-injection-enhanced defect-structure transformation for the deep hole-trap centers introduced by γ-ray irradiation of p-type InP. Low-temperature γ-ray irradiation and subsequent minority-carrier injection is found to cause a marked enhancement of the defect-structure transformation from a major deep hole trap at $E_v+0.32$ eV to a deeper hole-trap center at $E_v+0.52$ eV. This phenomenon reveals two new factors in defect reaction processes: (i) the important role of an anion-displacement defect as a nonradiative recombination center as well as deep carrier-trap center,[3,4] and (ii) electrically induced long-distance defect migration in III-V semiconductors. Here, we focus our attention on demonstrating the first property and the origin of the defect through the electronic reaction processes. Direct evidence is shown to indicate the role of the major radiation-induced hole trap (0.32 eV) as an efficient nonradiative recombination channel using the double carrier-pulse deep-level transient spectroscopy (DLTS) technique.[5] This result was confirmed by observation of a prominent photoluminescence (PL) recovery due to photoinjection annealing of this center. Strong electron-phonon coupling for the 0.32-eV level was also evidenced by optical measurements, demonstrating a recombination-enhanced mechanism[3-4,6] for the electronic defect reaction here.

The n^+-p or Schottky diode samples used in this study were prepared from zinc-doped Czochralski-grown p-type InP single crystals. Diodes were formed by thermal S diffusion into p-type substrates with carrier concentrations of 3×10^{15}–3×10^{17} cm^{-3}. Defects were introduced by γ-ray irradiation at both 80 and 300 K. The deep-level properties and reaction kinetics were studied using extended capacitance transient spectroscopy techniques [double-carrier pulse DLTS,[5] isothermal capacitance transient spectroscopy (ICTS)], photocapacitance (PHCAP), and PL measurements.

A typical DLTS spectrum for 80-K γ-ray-irradiation-induced deep hole traps in p-type InP ($p=3\times10^{15}$ cm^{-3}) and the spectrum change following thermal anneals up to 380 K are shown in Fig. 1(a). The dominant level (labeled $H4$) is also observed after high-energy electron irradiations,[7-9] and has a hole thermal emission activation energy of 0.37 eV. This level is found to exhibit a strong temperature dependence for hole capture in the 150–250 K region, where $\sigma(T)=4\times10^{-16}\exp(-50\pm15\ \text{meV/kT})$. The exponential temperature dependence suggests a multiphonon-emission hole-capture process that will be discussed in a later section. The activation energy of about 50 meV could correspond to the hole-capture barrier height in the configuration coordinate and thus one can evaluate the defect energy level of this center as $E_v+0.32$ (±0.015) eV.

Under the zero-biased junction condition this defect is stable up to 280 K [region I in Fig. 1(a)]. Remarkable spectral changes were observed after thermal (DLTS) scans in temperature region II (280–380 K). Here the 0.32-eV level is found to decrease rapidly. Instead, a new deeper hole-trap center at $E_v+0.52$ eV (labeled $H5$) tends to grow in correlation with the disappearance of the 0.32-eV level.

Isothermal annealings around 380 K provide an almost identical defect-reaction barrier height (1150 ± 45 meV) for both annihilation and growth reaction kinetics for the centers, and an extremely small pre-exponential factor ($\sim10^9$ sec^{-1}) for growth of the 0.52-eV defect. This suggests a long-distance defect motion in which on the order of $\sim10^5$ defect jumps (or reorientations) are required.

Marked enhancements and strong correlation with the defect-structure transformation were observed under forward-bias minority-carrier-injection conditions in temperature region I. Electrically enhanced reactions were monitored by ICTS measurements, shown in Fig. 1(b), where changes in both defect concentrations and reaction rates were detected simultaneously. In the initial injection-annealing stage with small current densities (≤450

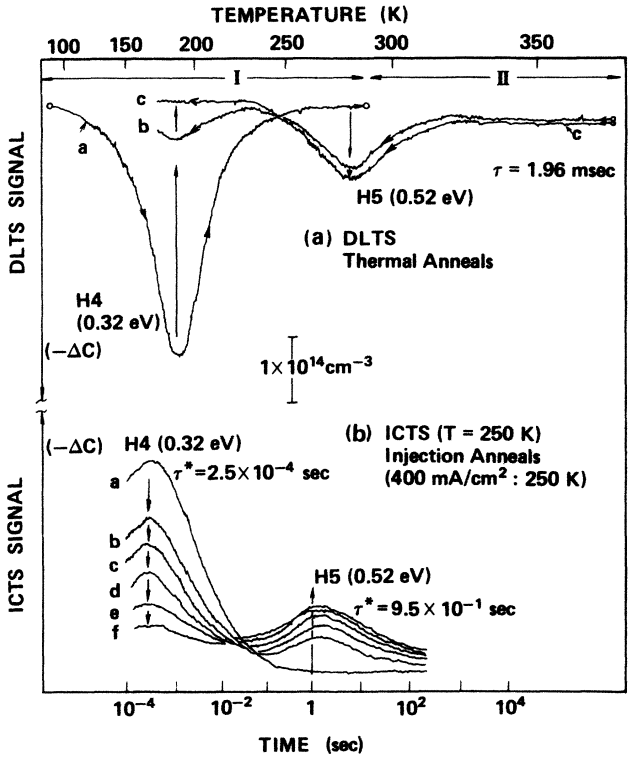

FIG. 1. (a) DLTS spectra of p-type InP ($p = 3\times10^{15}$ cm^{-3}) after γ-ray irradiation at 80 K and anneals up to 280 K (a). Shown also (b) and (c) are successive thermal anneals up to 380 K which reveal emergence of a new hole-trap level at 0.52 eV and disappeance of the major hole trap at 0.32 eV. (b) ICTS spectrum change for the two hole traps due to successive minority carrier injection (400 mA/cm^2) at 250 K for 0 (a), 30 (b), 60 (c), 90 (d), 120 (d), 150 (e), and 250 sec (f). τ^* (2.5×10^{-4} sec and 9.5×10^{-1} sec) are hole emission time constants for the 0.32-eV and the 0.52-eV levels, respectively.

mA/cm^2), we observed first-order reaction kinetics, described by a simple exponential formulation, versus the injection time period. We found a small but identical activation energy (125 ± 40 meV) for both the annihilation and growth processes. Minority-carrier injection is found to cause a substantial reduction of the defect-reaction barrier heights as compared to the thermal reaction process. The activation-energy difference between thermal and injection annealing exactly corresponds to the maximum energy liberated from electron-hole recombination at the 0.32-eV hole-trap center which is similar to the results observed in GaAs and GaP.[10]

In order to clarify the origin of the electronic enhancement, we have examined the optical and electronic characteristics of the relevant deep defect levels. We examined the optical transition on the 0.32-eV level by means of optical DLTS, PHCAP, and TSCAP measurements. An example of an optical DLTS signal (S^0) under dc excitation with an incident photon energy of 0.9 eV is shown in Fig. 2(a). The photoexcitation-induced capacitance transient signals $S^0(h\nu)$ were always detected in a lower temperature region than T_m, the DLTS peak temperature, where thermal hole-emission rates were negligibly small. This temperature-independent signal is due to an optical hole transition from the 0.32-eV level to the valence band, since the signal has disappeared after injection annealing of this center. This optical hole transition was also observed by both PHCAP and TSCAP measurements.

We have analyzed the optical ionization data based upon the theory deduced by Chantre, Vincent, and Vois,[11] where an electron-phonon interaction is taken into account in the limit of the strong electron-phonon coupling. We could obtain a good fit of the optical cross-section spectra to the theory with E_0 (optical threshold energy) $=0.68$ eV and d_{FC} (Frank-Condon shift) $=0.35$ eV (see Ref. 13). Large E_0 and d_{FC} are consistent with the presence of the hole-capture barrier (-50 meV) derived above, indicating a strong lattice relaxation at the 0.32-eV level defect.[12,13]

Direct evidence was obtained to demonstrate the role of the 0.32-eV level as a nonradiative recombination center using double-carrier pulse DLTS measurements. Here, we added minority-carrier (electron) injection pulses to normal majority-carrier (hole) pulses to examine electron capture by this defect center. Figure 2(b) shows a comparison of DLTS spectra observed under normal pulse condition a and double carrier pulse conditions b and c. One can see a distinct reduction of the signal peak height (hole emission) from the 0.32-eV level in conditions b and c. This implies efficient electron capture by this center as

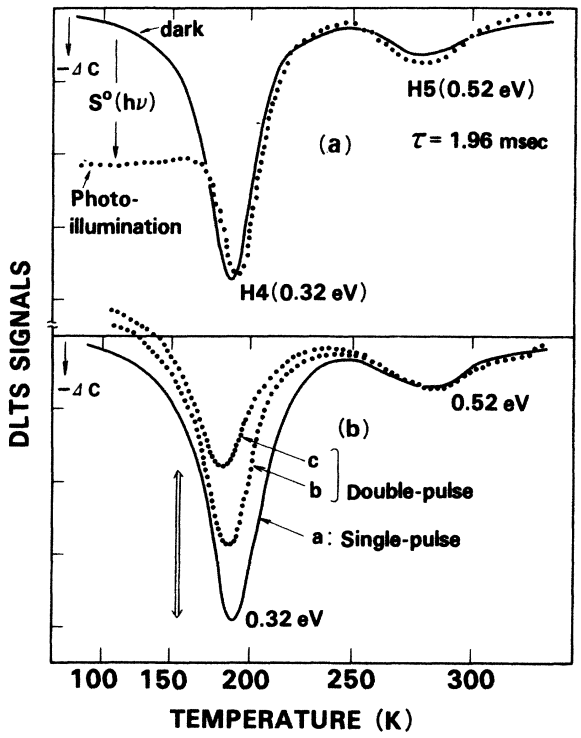

FIG. 2. (a) Optical DLTS spectrum under photo-illumination ($h\nu=0.9$ eV). Temperature-independent signal $S^0(h\nu)$ originates from optical hole transition from the 0.32-eV level to valence band. (b) Comparison of the DLTS spectrum under two different carrier pulse conditions: a single carrier (hole) pulse to fill the traps by hole, b and c double carrier pulse to fill the traps by both hole and electrons. Here, 5 μsec minority-carrier injection pulses with current density of 120 mA/cm^2 (b) and 200 mA/cm^2 (c) are added to the single hole pulse of (a).

well as simultaneous hole capture, resulting in nonradiative recombination at this center. In this experiment, we have observed that the DLTS peak heights of the 0.32-eV level tend to decrease with increase in the minority-carrier-injection densities, shown in Fig. 2(b). These results demonstrate the role of the 0.32-eV hole-trap center as an efficient nonradiative channel under excess-minority-carrier-injection conditions.

This conclusion was reinforced by the observation of photoluminescence (PL) efficiency recoveries due to photoinjection annealing of the 0.32-eV-level defect, shown in Fig. 3. In this experiment, γ-ray irradiation and subsequent photoexcitation (Ar laser, 5145 Å) with 6 W/cm^2 were performed in Schottky-diode p-type samples with semitransparent Au film. As-irradiated samples showed a weak luminescence spectrum at 77 K, including two well-assigned peaks: donor–valence-band (1.42 eV) and conduction-band–acceptor (1.38 eV) radiative transitions. Marked recovery of the 1.42-eV peak intensity was observed after 300-K photo-excitation (injection), where the 0.32-eV level defect was found to decrease by photo-injection-enhanced annealing. The result indicates that the degradation and marked recovery of the radiative-transition (1.42 eV) efficiency can be attributed to the introduction and disappearance of an efficient nonradiative recombination channel, detected as a deep hole-capture and -emission center of the 0.32-eV level here.[14] This is understood by considering the two competing transition channels under the presence of excess minority carriers in p-type materials. These results rule out the possibility of a charge-state effect[15] or an alternative saddle-point mechanism (Bourgoin mechanism[16]), and demonstrates a recombination-enhanced reaction mechanism[3,4,6] for the electronic defect-structure transformation studied here.

It should be noted here that the recovery of the 1.38-eV peak intensity is prominently suppressed in spite of the disappearance of the 0.32-eV level defects. This could provide an insight into the origin of the secondary defect of the 0.52-eV deep hole trap. In room-temperature γ-ray or electron irradiation, this center is always detected in heavily zinc-doped samples that have not received injection annealing. The concentrations are also found to increase with an increase in zinc concentration.[14] These results together with the new results presented here, provide evidence that this center is related to a complex defect of substitutional zinc, combined with the 0.32-eV defect species. This complex center does not work as a radiative center but as a normal deep hole-trap center.

The defect structure of the major radiation defect of the 0.32-eV level has been addressed in several theoretical and experimental studies performed in low-temperature electron irradiations.[8,17,18] A common feature in the accumulated data is an anion-displacement defect, which is selectively produced by high-energy electron bombardment. The exact structure is now difficult to determine, but a note should be made of a related characteristic of this center; this center is originally a positively charged donor which effectively compensates shallow acceptors. The recent theoretical and experimental studies on anion-antisite or anion-interstitial-related defects (interstitial-vacancy Frenkel pair) in III-V semiconductors suggest the interesting roles of these centers, as single or double donors and also as nonradiative recombination centers.[19-21] The inherrent characteristics match those demonstrated here. We, therefore, tentatively assign 0.32-eV level to a $+ \rightarrow 2+$ thermal transition at the anion–interstitial-vacancy Frenkel pair (or antisite). The defects with positive charge state (singly ionized donors) are then considered to serve both as deep hole traps ($+ \rightarrow 2+$ transition) and as efficient nonradiative recombination channels accompanied by strong multiphonon emission.

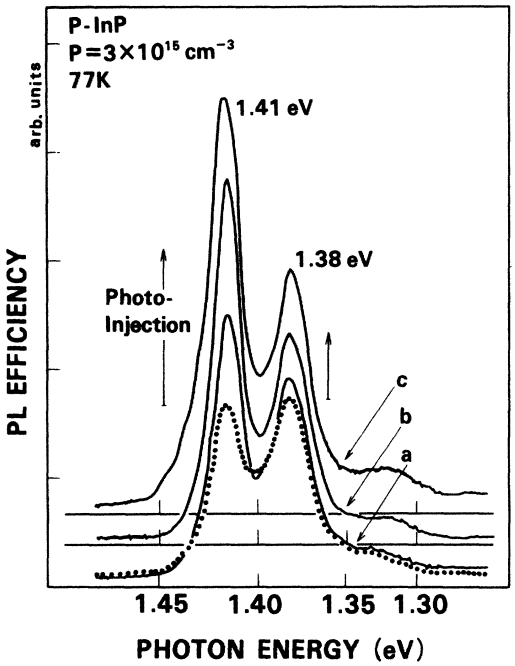

FIG. 3. PL efficiency recovery due to photoinjection enhanced annealing of the 0.32-eV level defect in p-type InP ($p = 5\times10^{15}$ cm^{-3}) with semitransparent Au film on the surface. Dotted curve is for as-γ-ray irradiated sample, and spectra a–c are observed after 300-K photo-injection annealing using Ar laser (5145 Å, 6 W/cm^2) excitations at 30, 65, and 200 sec, respectively.

In summary, we have presented the first observation of a minority-carrier-injection-enhanced defect-structure transformation in low-temperature γ-ray irradiated p-type InP. Direct evidence is shown to demonstrate the role of the major radiation defect center as a nonradiative recombination channel with strong electron-phonon coupling as well as a deep hole-trap center of the 0.32-eV level. Our results have firmly established the recombination enhanced mechanism for the electronic defect reactions here and suggest an important role of anion-displacement defects in nonradiative recombination processes in III-V compound semiconductors. Work is continuing to further elucidate the microscopic processes using EPR and optically detected magnetic resonance studies.

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