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Effect of Er dopant on the properties of $In_{0.53}Ga_{0.47}As$ layers grown by liquid phase epitaxy

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Detailed properties of $In_{0.53}Ga_{0.47}As$ layers grown by liquid phase epitaxy from melts containing 0.04 and 0.1 wt % Er are reported. The carrier concentration in the material is reduced by almost two orders of magnitude as a result of Er doping. Low temperature photoluminescence measurements indicate that both the donor and the acceptor type impurities are gettered by Er and the full-width at half-maximum of the major peak is reduced to 4 meV for the layer with the highest Er doping. From deep level transient spectroscopy experiments on undoped layers, we confirm the presence of an electron trap with activation energy of 0.17 eV. Density of this trap is reduced by more than two orders of magnitude in the Er doped material and another electron trap with activation energy of 0.15 eV is revealed from the analysis of the experimental data. We associate the 0.17 eV trap with impurities in the material. From low temperature photoconductivity and photocapacitance experiments, we further confirm that Er creates a level located 40 meV above the valence band. Density of this center increases in the material after high temperature annealing. We suggest that the Er-related level is due to Er atoms occupying cation sites in the material and acting as an isoelectronic impurity. © *1997 American Institute of Physics.* [S0021-8979(97)00905-5]

I. INTRODUCTION

Doping of III–V compound semiconductors with the rare earth element Er is an interesting area of research today. Er atoms, incorporated in the host semiconductor, give rise to sharp luminescence at 1.54 μm due to intracenter transitions of an incomplete or partially filled $4f$ level.[1–6] This emission wavelength exactly coincides with the minimum loss region of present day silica based optical fibers. Hence it is felt that wide band gap semiconductors such as GaAs, InP, and InGaAsP, doped with suitable amounts of Er, could be used for making sources for long distance optical communications. An additional advantage of adopting this route is the observed fact that Er related emission wavelength is highly stable with changes in temperature.[2] Light emitting diodes based on various III–V compounds have already been fabricated and reported.[7–11] The second important and attractive property of Er is its ability to reduce impurities in layers, grown by liquid phase epitaxy (LPE), through the formation of insoluble complexes in the growth melt.[6] This property has been used for the growth of high purity LPE $In_{0.53}Ga_{0.47}As$ layers for the fabrication of superior performance PIN photodiodes.[12] However, Er and other rare earth dopants are also known to produce isoelectronic traps.[13–17] Deep traps, in general, have some undesirable effects on the operation of devices such as limiting the speed of photodiodes and reducing the luminescence efficiency of optical sources. Therefore, before judging the suitability of a material for a particular device application, it is necessary to have a full knowledge of the deep levels present in the same. Er doped $In_{0.53}Ga_{0.47}As$ is a material where, to our knowledge, no such study has been made. We thus chose to investigate the effect of Er doping on both the shallow level impurities and the deep level defects in $In_{0.53}Ga_{0.47}As$ layers grown by LPE. Experimental data were collected through the applications of Hall effect, photoluminescence (PL), photoconductivity, photocapacitance, and deep level transient spectroscopy (DLTS) techniques. The details of our work and the results are being presented in this article.

II. MATERIALS GROWTH

Layers having thicknesses of 6–8 μm were grown in our laboratory on semiinsulating InP substrates, oriented in the ⟨100⟩ direction, using a horizontal sliding boat LPE reactor. All the components of growth were of 99.9999% purity. Further purification was done by first baking the In metal alone in the LPE reactor at 750 °C for 10–15 h, followed by baking the growth melt at 700–720 °C for 20–25 h. After this baking procedure, the required amount of Er was added to the growth melt and baked further at 750–760 °C for 6 h. Growth was typically done at 637–638 °C using a melt supersaturation of 3 °C and a cooling ramp of 0.1 °C/min. A quick *in situ* etching of the InP substrate with pure In was always done before growth. Both baking and growth were done under Pd-diffused hydrogen flow. Er doped layers were grown from melts containing either 0.04 or 0.1 wt % Er. From physical observations, the surfaces of all the layers looked smooth and mirror polished.

III. CHARACTERIZATION

The mobility and the carrier concentrations of both undoped and Er doped layers were measured by the van der Pauw Hall technique. The samples were typically 5 mm×5 mm squares with alloyed In–Sn ohmic contacts applied at the four corners. The undoped layer was characterized both

TABLE I. Mobility and carrier concentrations of undoped and Er doped $In_{0.53}Ga_{0.47}As$ layers grown by liquid phase epitaxy.

Er content in growth melt (wt %)	Conductivity type	Electron mobility (cm^2/Vs) 300 K	77 K	Carrier concentration at 300 K (cm^{-3})
0	*n*	11 100	38 000	2×10^{15}
0.04	*n*	12 000	-	8×10^{13}
0.1	*n*	12 500	-	5×10^{13}

at 300 K and 77 K. Hall measurements could not be done at 77 K on the Er doped layers due to their very high resistivities at low temperatures.

Photoconductivity measurements were done at 12 K on small bar-shaped samples with ohmic contacts applied at two ends. The sample was mounted on the cold finger of an APD Cryogenics Displex closed-cycle helium cryostat, provided with a quartz window for illumination from outside. Illumination of the layer surface was done in the photon energy range of 0.62–0.85 eV, obtained from an Oriel 0.25 m monochromator, coupled with a stabilized xenon arc lamp. Both the biasing of the photoconductor and the photocurrent measurement were done using a Keithley model 236 Source-Measure unit. The resultant data were normalized with respect to the intensity variation of the different spectral components of the optical source. Photoconductivity measurements were done on both undoped and Er doped samples. Only the 0.1% Er doped layer was used in this study. Further, one part of the Er doped layer was cut and annealed at 740 °C for 40 min under hydrogen flow. Experimental data were collected on the as-grown, as well as on the annealed layer.

PL measurements were done at 8 K in a standard setup at Tata Institute of Fundamental Research, Bombay comprised of an Ar^+ ion excitation laser, a 0.67 m analyzing monochromator, and the conventional lock-in detection system.

Photocapacitance measurements were done on semitransparent gold Schottky barrier diodes of 0.5 mm diam, formed on clean layer surfaces by electron beam evaporation. In order to enhance the Schottky barrier height, a thin native oxide film was grown on the layer surface by a special pretreatment.[18] The same diodes were used for doing the DLTS measurements in the temperature range 100–350 K. Details of our photocapacitance and DLTS systems may be found in previous publications.[19,20]

IV. RESULTS

A. Carrier transport data

The carrier concentration and Hall mobility of undoped and Er doped $In_{0.53}Ga_{0.47}As$ layers are presented in Table I. The impurity gettering effect of Er is very much evident from these experimental data which show that the residual carrier concentration in the material is decreased by about two orders of magnitude upon addition of only 0.1 wt % Er to the growth melt. It is also interesting to note that the layers remained *n*-type even when the residual carrier concentration is dropped to 5×10^{13} cm^{-3}. This observed fact indirectly states that both donor and acceptor type impurities are reduced in the material as a result of Er doping.

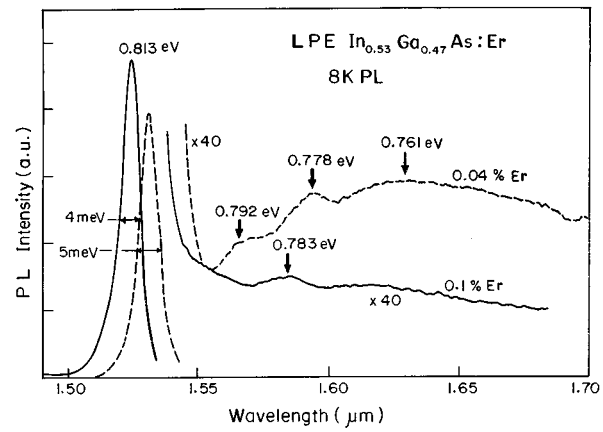

FIG. 1. 8 K PL spectra for Er doped $In_{0.53}Ga_{0.47}As$ layers grown from melts containing 0.04 and 0.1 wt % Er.

B. Photoluminescence

Figure 1 shows the PL spectra for Er doped layers. Each spectrum is dominated by a major peak at about 0.81 eV, representing donor levels to valence band transitions and donor levels to acceptor levels transitions. The full-width at half-maximum (FWHM) for the low-Er layer is extremely narrow at 5 meV which is further reduced to 4 meV in the material grown from a higher Er content melt. This result is a direct indication of gettering of donor type impurities by Er.[21] The shift of this peak towards higher energies as a result of the increase in Er doping, was observed earlier in LPE grown InGaAsP and the effect was attributed to small changes in material composition due to the formation of microparticles of Er complexes.[21] Other than the main peak, we note three very weak peaks at 0.792, 0.778, and 0.761 eV in the low-Er layer. The peak at 0.792 eV is readily identified with Zn acceptor level while that at 0.761 eV represents its LO-phonon replica.[22] The peak at 0.778 eV may similarly be related to transitions from donor levels to Si acceptor levels. In contrast to results obtained on Er doped InGaAsP,[21] we note that the acceptor related peaks are decreased here as the Er content in the growth melt is increased from 0.04 to 0.1%. This perhaps explains why the layers remained *n*-type after Er doping.

C. Photoconductivity

In Fig. 2, we present the photoconductivity data obtained on the undoped layer as well as on the Er doped as-grown and annealed layers. An initial rise at around 0.66 eV is observed in all cases and is attributed to transitions from a deep level. From the expression of Towe,[23] we calculate the band gap of $In_{0.53}Ga_{0.47}As$ to be around 0.818 eV at 12 K and hence the depth of this level is about 0.16 eV. From photoconductivity measurements it is, however, not possible to ascertain whether it is an electron or a hole trap. In the higher energy region of the spectra, we note several other transitions

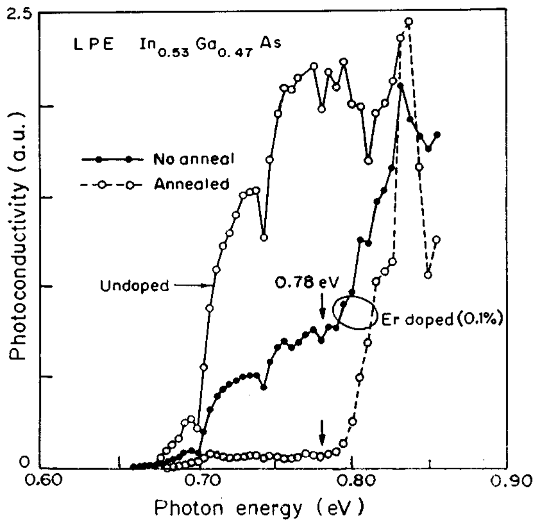

FIG. 2. Photoconductivity spectra obtained at 12 K for the undoped and the Er doped $In_{0.53}Ga_{0.47}As$ layers. The Er doped layer was grown from a melt containing 0.1 wt % Er; the data for both the as-grown layer and the annealed layer are presented.

due to various shallow acceptor levels present in the material. However, the most important feature is the sharp photoconductivity increase at 0.78 eV photon energy which is observed for the Er doped layers only. Further, the relative intensity of this photoconductivity signal is stronger in the annealed layer as compared to that obtained from the as-grown material. This step rise at 0.78 eV for the annealed material is shown more clearly in the expanded spectrum of Fig. 3 where we have also identified the other impurity related transitions from their respective energy positions. We thus observe that Er doping of LPE grown $In_{0.53}Ga_{0.47}As$ produces a new localized energy level in the band gap which gives rise to strong photoconductivity enhancement at 0.78 eV. From the difference of this energy with the 12 K band

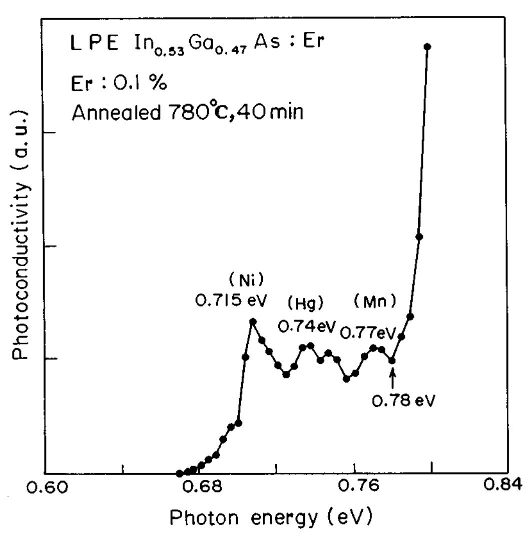

FIG. 3. The expanded form of the photoconductivity spectrum of the annealed Er doped layer showing peaks due to various acceptor levels in the material and the transition at 0.78 eV.

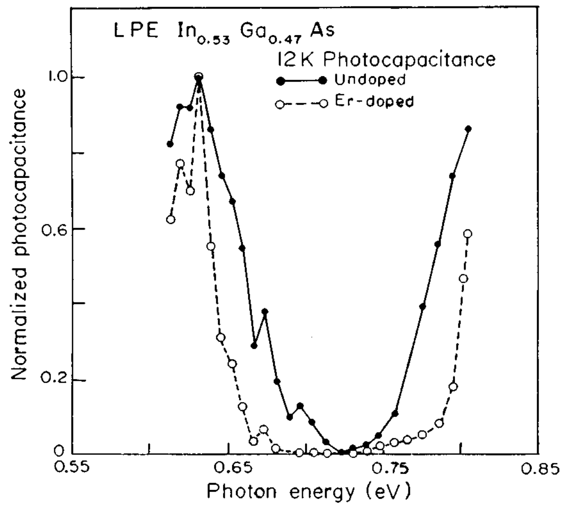

FIG. 4. Photocapacitance spectra for the undoped and the as-grown Er doped layers.

gap of $In_{0.53}Ga_{0.47}As$, we calculate the depth of this level to be around 40 meV with respect to the nearest band edge.

D. Photocapacitance

The photocapacitance spectra for the undoped and the as-grown Er doped layers of Fig. 2 are presented in Fig. 4. For both the materials, we identify, capacitance falling thresholds at 0.64 and 0.67 eV and they may be attributed to complimentary transitions from two electron traps located at 0.17 and 0.15 eV, respectively, below the conduction band edge. This observation may further be related to the photoconductivity rise at 0.66 eV shown in Fig. 2. The gradual capacitance rise in the undoped material from 0.73 eV photon energy may be related to the electron transfer from various acceptor levels to the conduction band. The Er doped material, on the other hand, shows a drastic fall in the relative magnitudes of such transitions, whereas a sharp increase in photocapacitance at a photon energy of 0.78 eV is observed. This result is very much similar to what we obtained from the photoconductivity experiments and the presence of the Er related 40 meV level is further supported. Since the capacitance increases at this energy, we can clearly and conclusively identify the level as an acceptor, located near the valence band.

E. Deep level transient spectroscopy

Figure 5 shows the DLTS spectra for the undoped as well as the as-grown Er doped samples, grown from melts containing 0.04 and 0.1 wt % Er. The single sharp peak, observed for the undoped material, is identified with an electron trap and from the usual Arrhenius plot in Fig. 6, we find that the activation energy of this trap is 0.17 eV. For the Er doped materials, the DLTS peak is relatively broad and is shifted towards lower temperatures. The DLTS peak heights for both kinds of Er doped layers are almost equal and are more than two orders of magnitude smaller than those for the undoped material. The broadness of the DLTS peaks for the Er doped samples makes Arrhenius-plotlike analysis difficult

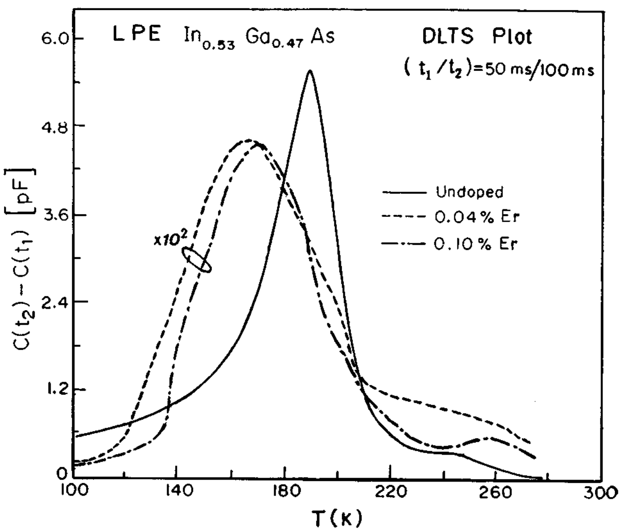

FIG. 5. DLTS spectra for undoped and Er doped $In_{0.53}Ga_{0.47}As$ layers. The Er doped layers were grown from melts containing 0.04 and 0.1 wt % Er.

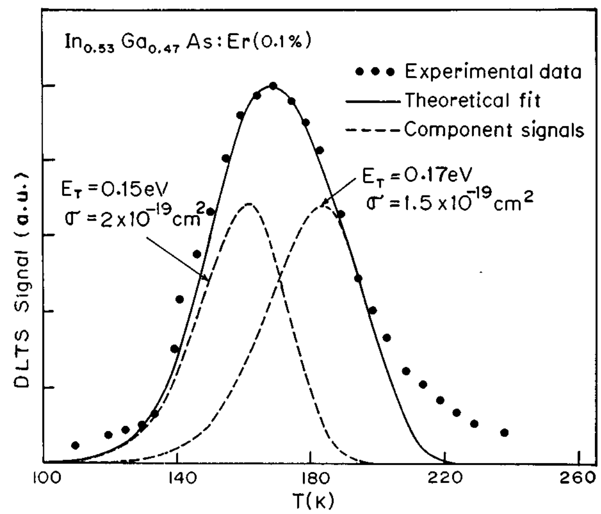

FIG. 7. Theoretical fit to the experimental DLTS data, obtained on the Er doped $In_{0.53}Ga_{0.47}As$ layer, grown from melt having 0.1 wt % Er. Theoretically calculated DLTS peaks for the two component electron traps are shown with their assumed parameters.

and we, instead, analyzed the result by a theoretical curve fitting technique. Figure 7 shows that a good theoretical fit with the experimental data can be obtained by assuming the presence of two electron traps with activation energies of 0.17 and 0.15 eV. The temperature position of the resolved peak for the 0.17 eV level approximately coincides with that obtained experimentally for the undoped layer. Further, the observed low temperature tail of the DLTS peak for the undoped layer may be due to the presence of the 0.15 eV trap in relatively smaller concentrations.

V. DISCUSSION AND CONCLUSIONS

From Hall effect measurements we find that Er is a very effective gettering agent for LPE grown $In_{0.53}Ga_{0.47}As$. The presence of a small amount of Er in the growth melt can drastically reduce the background concentration in the grown layer. From PL experiments we further note that both donor and acceptor type impurities are gettered by Er and the FWHM of the material almost reaches the theoretical limit.

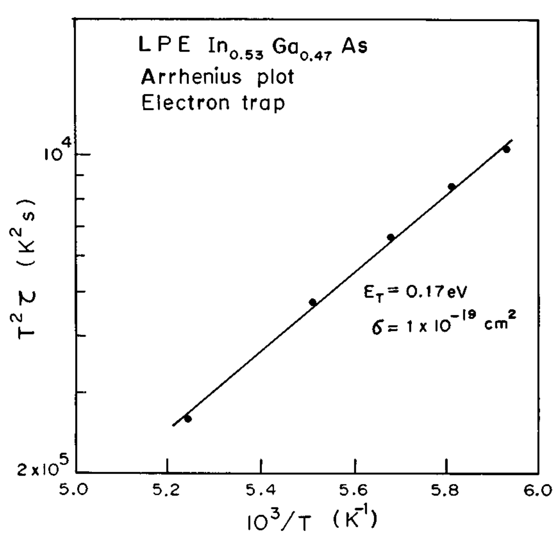

FIG. 6. Arrhenious plot for the electron trap, observed in the undoped $In_{0.53}Ga_{0.47}As$ layer.

Two electron traps having activation energies of 0.15 and 0.17 eV are conclusively identified in the material from both photocapacitance and DLTS experiments. Previous DLTS data on LPE $In_{0.53}Ga_{0.47}As$ confirmed the existence of a single electron trap whose activation energy was reported as either 0.17 eV[24] or 0.16±0.01 eV.[25] Our data suggests that the material perhaps contains two electron traps with activation energies between 0.15 and 0.17 eV. As for the origin of these traps in LPE $In_{0.53}Ga_{0.47}As$, no clue is available from the literature. However, we can note from the DLTS data of Fig. 5 that Er has a very pronounced effect in reducing the density of the 0.17 trap. This suggests that the trap is related to some impurities in the material which are gettered by Er in the growth melt. Similar origin was previously attributed to a 0.16 eV electron trap, detected in $In_{0.53}Ga_{0.47}As$ layers grown by molecular beam epitaxy.[26] As for the 0.15 eV electron trap, no evidence for gettering by Er is available from our data. Taking into consideration the low temperature tail of the DLTS plot for the undoped layer, we can only say the Er gettering effect is perhaps present for the 0.15 eV electron trap as well so that the same impurity related source may be attributed to this trap.

The other important effect of Er on LPE grown $In_{0.53}Ga_{0.47}As$ is the creation of an acceptor level, located 40 meV above the valence band. This we get conclusively from both photoconductivity and photocapacitance experiments. We also note that the density of this center apparently increases after a high temperature annealing process. For a sufficiently high doping density of Er, many of the Er atoms sit at interstitial positions. During high temperature anneal, some of them move towards substitutional sites in the host crystal lattice. If we associate the 40 meV center with an Er atom placed at the substitutional site, then its increase with annealing can be explained. A similar effect of annealing was previously reported for a 35 meV hole trap in Er doped GaAs grown by LPE and it was attributed to an isoelectronic Er_{Ga} center.[17] On the other hand, the Er_{In} center in Er doped InP gave rise to electron traps.[27,28] Since we are getting a shallow hole traplike center in our material, all we can say is that it is an isoelectronic trap due to Er atoms placed at the cation sites.

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