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Investigation of Deep Levels in $In_{1-x}Ga_xP$ Grown by Liquid Phase Epitaxy

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Deep levels in undoped *n*-type $In_{0.5}Ga_{0.5}P$ and $In_{0.3}Ga_{0.7}P$ grown on GaAs and GaAsP substrates by liquid phase epitaxy (LPE) is investigated. Only one kind of deep electron trap is observed from the deep-level transient spectroscopy (DLTS) measurements. Its apparent ionization energy, including the capture barrier energy, is about 0.27 eV, irrespective of the Ga composition. The DLTS spectra, dependent on the pulse time and the electric-field magnitude, show a large alloy broadening. The concentration of traps in $In_{0.3}Ga_{0.7}P$ is larger than that in $In_{0.5}Ga_{0.5}P$, and the capture barrier of traps in $In_{0.3}Ga_{0.7}P$ is smaller than that in $In_{0.5}Ga_{0.5}P$. The persistent photoconductance phenomenon is confirmed in the $In_{0.3}Ga_{0.7}P$ samples. The DX-like nature of the traps is discussed by comparing the observed characteristics with the characteristics of DX centers in $Al_xGa_{1-x}As$. From the secondary ion mass spectroscopy analysis, the impurity causing the DX center in LPE-grown undoped *n*-$In_{1-x}Ga_xP$ is attributed to sulfur.

I. INTRODUCTION

Ternary $In_{1-x}Ga_xP$ is a direct band gap semiconductor in the range of $0<x<0.74$, which has a maximum band gap energy of 2.2 eV at 300 K (570 nm in wavelength).[1] High-quality epilayers of $In_{0.5}Ga_{0.5}P$ and $In_{0.3}Ga_{0.7}P$ can be grown on commercial GaAs and GaAsP substrates by the liquid phase epitaxy (LPE) method.[2,3] Because of the applicability of $In_{1-x}Ga_xP$ for light emitting diodes,[2,4] laser diodes,[5] and other electrical devices,[6] deep levels in this material have been extensively studied in recent years.[7-9] It is argued that the origin of the deep levels in $In_{1-x}Ga_xP$ is related to a phosphorous vacancy caused by the high vapor pressure of phosphorous.[10,11] It has been recently reported, however, that the deep levels in this material show DX-like properties.[8,9,12,13] Since $In_{0.3}Ga_{0.7}P$ is an attractive candidate for yellow light sources, detailed information about the deep levels in $In_{0.3}Ga_{0.7}P$ epilayers is needed.

In this paper, we report the properties of the deep levels in $In_{1-x}Ga_xP$, with the Ga composition of $x=0.5$ and 0.7 investigated by using the deep-level transient spectroscopy (DLTS) method. The DX-center nature of the deep levels in $In_{1-x}Ga_xP$ is clarified by the difference of the electric properties for the deep levels in $In_{0.5}Ga_{0.5}P$ and in $In_{0.3}Ga_{0.7}P$ and by the persistent photoconductance (PPC) phenomenon observed in $In_{0.3}Ga_{0.7}P$. The secondary ion mass spectroscopy (SIMS) analysis reveals that the observed DX center originates from the residual sulfur impurities.

II. EXPERIMENTAL

Undoped *n*-$In_{0.5}Ga_{0.5}P$ and *n*-$In_{0.3}Ga_{0.7}P$ epilayers were grown on (100) n^+-GaAs and (100) *n*-$GaAs_{0.6}P_{0.4}/n^+$-GaAs substrates, respectively, by the LPE method. The details of the growth technique have been published elsewhere.[14] The net electron concentrations in the undoped $In_{1-x}Ga_xP$ was estimated to be about 10^{16} cm^{-3}~10^{17} cm^{-3} from C-V measurements. The DLTS measurements were performed with the Schottky diodes fabricated on these materials. For ohmic contacts, AuGe/Ni/Au were evaporated on the back sides of samples and then annealed at 350℃ for 2 min in a N_2 atmosphere. The Schottky contacts were formed on the surfaces of the samples by thermal evaporation of Au with an area of 0.196 mm^2 or 0.071 mm^2 under a vacuum of about 10^{-6} Torr. Before metal evaporation, the samples were etched with a HCl : H_2O (1 : 2) solution to eliminate the native oxide layer. The ideality factor of the fabricated Schottky diodes was in the range of 1.1~1.2.

The measurements of the capacitance for the DLTS and thermally stimulated capacitance (TSCAP) experiments were performed with a HP 4280A capacitance meter. The current-voltage characteristics of the diodes were measured by using a Keithley 236 Source Measure

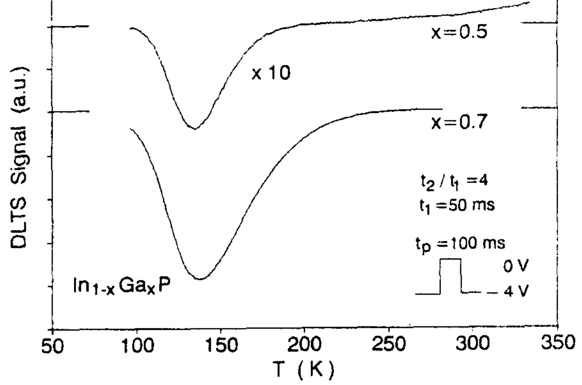

Fig. 1. Typical DLTS spectra of the $In_{0.5}Ga_{0.5}P$ # 1 and $In_{0.3}Ga_{0.7}P$ # 4 samples (see Table 1). From a comparison of the peak values of the DLTS spectra, it is clear that the concentration of deep traps in $In_{0.3}Ga_{0.7}P$ is larger than that in $In_{0.5}Ga_{0.5}P$.

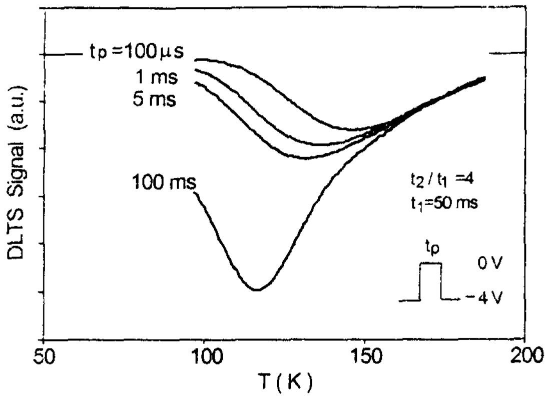

Fig. 2. DLTS spectra of the $In_{0.3}Ga_{0.7}P$ # 5 sample for a pulse time of 100 ms, 5 ms, 1 ms, and 100 μs. As the pulse time t_p is reduced, the temperature of the DLTS peak is shifted to a higher value.

Unit. The temperature scan in the DLTS and TSCAP measurements was made in the temperature range between 80 K (50 K for TSCAP) and 400 K at a heating rate of 2℃ /min. The PPC phenomenon was verified by the remnant photocapacitance after a white light source has illuminated the diodes. Samples were put under dark conditions more than 30 min after the exposure of the diodes to the light before taking the TSCAP trace. The SIMS analysis was performed with the aid of Charles Evans and Associates.

III. RESULTS AND DISCUSSION

1. Properties of Deep Levels in $In_{1-x}Ga_xP$

Figure 1 shows typical DLTS spectra of $In_{0.5}Ga_{0.5}P$ and $In_{0.3}Ga_{0.7}P$ for an emission rate of 9.26 s^{-1}. The measurement conditions are a refilling pulse-time t_p of 100 ms, a refilling bias V_p of 0 V, and a measurement bias V_m of −4 V. The ratio of the two gate times t_2/t_1 is 4 and t_1 is 50 ms. As can be seen in this figure, only one kind of deep electron trap is observed in the temperature range from 80 K to 400 K. The apparent ionization energy E_T was estimated to be about 0.27 eV, irrespective of the Ga composition, from the Arrhenius plot of the emission rates. The capture cross sections were about 6.0×10^{-14} cm^2 for $In_{0.5}Ga_{0.5}P$ and 2.0×10^{-14} cm^2 for $In_{0.3}Ga_{0.7}P$. Since the DLTS spectrum for $In_{0.5}Ga_{0.5}P$ was multiplied by a factor of 10, this figure shows clearly that the concentration of the deep traps in $In_{0.3}Ga_{0.7}P$ is larger than that in $In_{0.5}Ga_{0.5}P$. The concentrations of deep traps in $In_{0.5}Ga_{0.5}P$ were always about 1.5×10^{15} cm^{-3} for all the samples, and those in $In_{0.3}Ga_{0.7}P$ were in the range of 1.0×10^{15} cm^{-3}~4.0×10^{16} cm^{-3}, depending on the samples (see Table 1).

Typical pulse-time dependence of the electron emission rate from the traps is shown in Fig. 2. The temperature of the DLTS peak is shifted to a higher value as the refilling pulse-time t_p is reduced, maintaining other measurement conditions the same. This tendency, observed in both the $In_{0.5}Ga_{0.5}P$ and $In_{0.3}Ga_{0.7}P$ samples, implies that the observed trap is composed of deep traps with different activation energies and that a fluctuation of the capture cross section is present. Because the electron capture of the traps with smaller capture cross sections must be suppressed by reducing the refilling pulse-time, the observed tendency implies that the deeper traps have larger capture cross sections.[10] As t_p is reduced from 100 ms to 100 μs, the apparent activation energy is increased from 0.26 eV to 0.41 eV, and the capture cross section is increased from 2.0×10^{-14} cm^2 to 7.0×10^{-11} cm^2 for $In_{0.3}Ga_{0.7}P$.

This trap also shows an enhancement of the electron emission rate by the electric field;[15,16] that is, the temperature of the DLTS peak is reduced as the refilling pulse-height is increased. The defect showing the above-

Table 1. Summary of free carriers and deep trap concentrations in $In_{1-x}Ga_xP$.

Sample		Carrier Con. (cm^{-3})	Trap Con. (cm^{-3})	Rel. Trap Con.	E_T (eV)
$In_{0.5}Ga_{0.5}P$	# 1	1.4×10^{17}	1.4×10^{15}	0.01	0.27
	# 2	4.7×10^{16}	1.4×10^{15}	0.03	0.26
$In_{0.3}Ga_{0.7}P$	# 3	4.8×10^{16}	4.2×10^{16}	0.87	0.25
	# 4	3.0×10^{16}	1.9×10^{16}	0.63	0.27
	# 5	1.1×10^{17}	4.0×10^{15}	0.04	0.26
	# 6	1.2×10^{16}	1.0×10^{15}	0.08	0.27

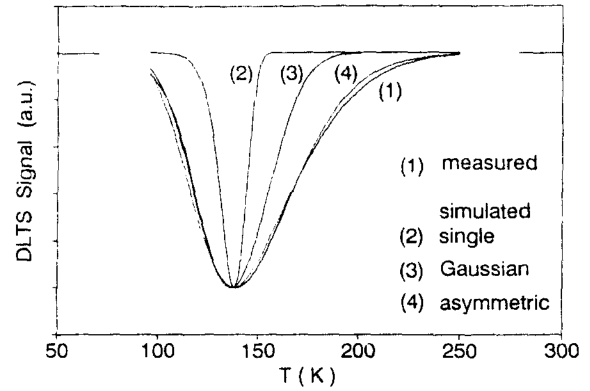

Fig. 3. Measured and simulated DLTS spectra for the $In_{0.3}Ga_{0.7}P$ #4 sample. The measured DLTS spectrum is broader than the simulated one under the assumption of single values of the activation energy and capture cross section.

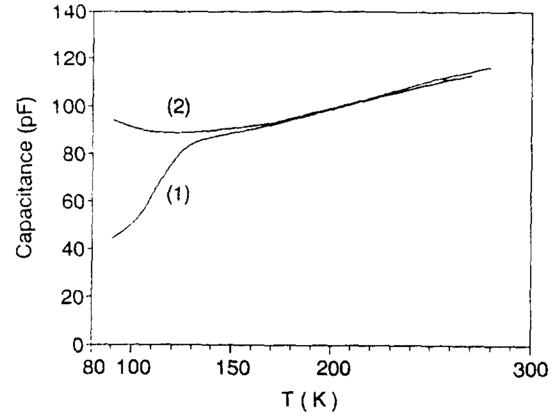

Fig. 4. Results of TSCAP measurements in the $In_{0.3}Ga_{0.7}P$ #3 sample. Curves (1) and (2) are the temperature-dependent capacitance values in a dark condition before and after the diode was exposed to white light, respectively. The difference between the two curves manifests the PPC effect.

mentioned characteristic features, such as pulse-time-dependent DLTS peak position, was observed in samples grown by various methods: LPE, metal-organic vapor phase epitaxy (MOCVD), metal-organic molecular beam epitaxy (MOMBE), etc.[7-9,13] However, the values of its ionization energy and capture cross section are quite scattered. From the results of the preceding paragraphs, it seems that such differences may be partially related to the difference of the employed pulse time and the built-in electric field in the junction due to the doping concentration of the sample, as was argued by Krynicki et al.[9]

Figure 3 shows typical fitting results of the measured DLTS spectrum of $In_{0.3}Ga_{0.7}P$. Spectrum (1) is the measured one, and curves (2), (3), and (4) are the simulated ones. Curve (2) is obtained by the values of the activation energy and capture cross section estimated from the Arrhenius plot of the emission rates. From the discrepancy between curve (1) and (2), it is evident that the activation energy is severely affected by the alloy broadening effect due to the random arrangement of the alloy atoms around the deep trap.[7,8,10] Curve (3) is simulated by assuming a Gaussian distribution for the trap concentration with respect to the activation energy E_T:[7,10]

$$N_T(E_T)dE_T = C\exp\left(-\frac{(E_T-E_T^0)^2}{2\Delta}\right)dE_T, \qquad (1)$$

where C is a normalizing constant, E_T^0 is the activation energy of the trap with the highest concentration, and Δ is the standard deviation of the activation energy. The measured DLTS spectrum can be best fitted with $\Delta = 33$ meV when we take E_T^0 and the capture cross section as the measured ones. For $In_{0.5}Ga_{0.5}P$, Δ is estimated to be 30 meV. It is not clear whether this rather small difference of the Δ values for $In_{0.5}Ga_{0.5}P$ and $In_{0.3}Ga_{0.7}P$ is caused by a real difference of the alloy broadening effect or by an inaccuracy in the DLTS method for the samples having large deep trap concentrations.[17] The discrepancy between curve (3) and the measured spectrum in the high-temperature region of Fig. 3 can be eliminated by assuming an activation-energy dependence or a temperature dependence of the capture cross section (curve (4) in this figure).[7,8]

2. Origin of Deep Levels in $In_{1-x}Ga_xP$

The PPC phenomenon, which is caused by the existence of the capture barrier of the trap,[19] is observed in the $In_{0.3}Ga_{0.7}P$ #3, #4 samples (see Table 1). In Fig. 4, curve (1) is the result of TSCAP measurements for the $In_{0.3}Ga_{0.7}P$ #3 sample under a dark condition. Curve (2) was obtained in a dark condition after the sample was exposed to white light at 50 K. As can be seen in this figure, the PPC effect exists for sample temperatures lower than 150 K. It has recently been established that the observed defect is responsible for the PPC effect.[9] In the case of the $In_{0.5}Ga_{0.5}P$ samples, the PPC effect was not observed. We believe, however, that this nondetection of the PPC effect in all the $In_{0.5}Ga_{0.5}P$ samples and the $In_{0.3}Ga_{0.7}P$ #5 and #6 samples is due to relative trap concentration (the ratio of deep-trap concentration to free-carrier concentration), which is too small as can be seen in the next paragraph.

When the capture barrier is present, the capture cross section σ_n for electrons can be expressed as

$$\sigma_n = \sigma_\infty \exp(-E_B/kT), \qquad (2)$$

where σ_∞ is the capture cross section at temperature $T = \infty$ and E_B is the capture barrier energy. The apparent thermal activation energy deduced from the emission rate e_n is the sum of the capture barrier energy and the energy difference between the conduction band minimum and the energy level of the deep trap. When the concentration of deep traps (N_T) is much lower than that of shallow donors (N_D), the DLTS peak value dC

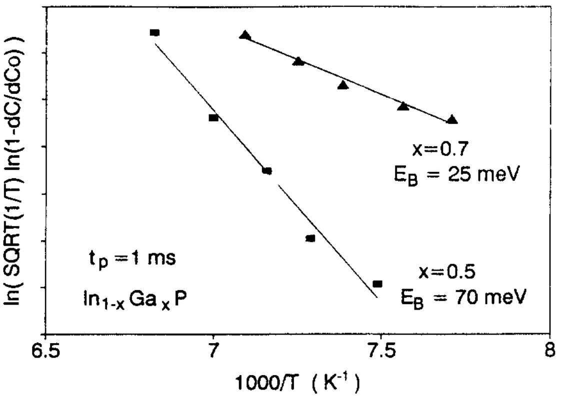

Fig. 5. Plot of the DLTS peak values dC (t_p= 1 ms) versus the inverse of the temperature. dC_0 is the peak value for a sufficiently large pulse time (t_p= 100 ms). The capture barrier E_B obtained from the slope is smaller in $In_{0.3}Ga_{0.7}P$ (# 5 sample) than in $In_{0.5}Ga_{0.5}P$ (# 1 sample).

varies with the pulse time t_p as

$$dC = S \times \frac{C_m N_T}{2N_D}\{1-\exp[-(c_n+e_n)t_p]\}, \tag{3}$$

where C_m is the capacitance at the measurement bias and S is a constant depending on the ratio of gate times $\gamma = t_2/t_1$ as

$$S = \gamma^{1/(1-\gamma)} - \gamma^{\gamma/(1-\gamma)}. \tag{4}$$

The electron capture rate c_n is related to the capture cross section by

$$c_n = \sigma_n v n, \tag{5}$$

where $v = (3kT/m^*)^{1/2}$ is the average thermal velocity of the electron and n is the concentration of electrons in the conduction band. Therefore, the capture barrier can be obtained from the variation of the DLTS peak value versus temperature in the pulse-time-dependent DLTS experiment (Fig. 5).[8,9] With t_p = 1 ms, the capture barriers are estimated to be about 70 meV for $In_{0.5}Ga_{0.5}P$ and 25 meV for $In_{0.3}Ga_{0.7}P$. When t_p is reduced to 100 μs, the barriers are found to be about 53 meV for $In_{0.5}Ga_{0.5}P$ and 30 meV for $In_{0.3}Ga_{0.7}P$. Even though the inaccuracy of the E_B values due to the t_p-dependent DLTS peak positions can not be neglected, it is clear that the barrier is smaller at the Ga composition of the direct-indirect band gap cross-over ($x \approx 0.7$).

Since the above-mentioned two phenomena are just the characteristics of DX centers in $Al_xGa_{1-x}As$,[18,19] they indicate that the observed electron trap may be due to an impurity atom which causes the DX center in $In_{1-x}Ga_xP$. Another characteristic feature of the DX centers in $Al_xGa_{1-x}As$ is that the concentration of the deep trap is maximized at the Al composition of the near band structure cross-over point with the same impurity concentration.[19] In Fig. 6, the relative deep trap concentrations in Table 1 are plotted versus the Ga composition x value. Even though the data points are scattered due to some difference in growth conditions, one can observe an evident tendency of increasing relative trap concentration as the x value is increased. It can, therefore, be safely inferred that the observed trap is a DX center originating from an impurity element.

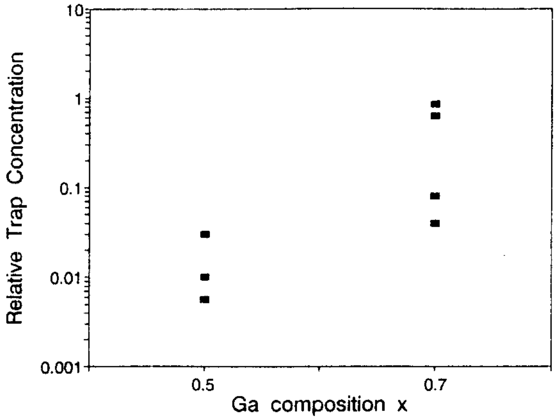

Fig. 6. Plot of relative trap concentration as a function of the Ga composition x for $In_{1-x}Ga_xP$. The relative trap concentration in $In_{0.3}Ga_{0.7}P$ is larger than that in $In_{0.5}Ga_{0.5}P$.

Table 2. SIMS data for impurity concentrations (atoms/cm ^{3}) in $In_{0.3}Ga_{0.7}P$ samples.

Sample	Si	Se	S
$In_{0.3}Ga_{0.7}P$ #4	1.9×10^{17}	$<1.5\times10^{14}$	6.8×10^{16}
$In_{0.3}Ga_{0.7}P$ #5	1.9×10^{17}	$<9\times10^{13}$	4.6×10^{15}

The DX-like traps responsible for the PPC effect were also observed in the samples of Si-doped $In_{0.5}Ga_{0.5}P$ grown by MOCVD (E_T=0.27 eV),[9] solution-grown Te-doped $In_{0.3}Ga_{0.7}P$ (E_T=0.4 eV),[8] Se-doped $In_{0.3}Ga_{0.7}P$ grown by chloride vapor-phase epitaxy (E_T=0.32 eV),[12] and S-doped $In_{0.3}Ga_{0.7}P$ grown by MOMBE (E_T=0.31 eV).[13] The values of the activation energy seem to depend on the nature of the dopants and on the experimental conditions of measurements.[9] Based on these dopants, we performed SIMS measurements for two $In_{0.3}Ga_{0.7}P$ samples showing very different defect concentrations (the ratio was about 10). Only Si, Se, and S were traced in the SIMS measurements, and the results are listed in Table 2. The concentrations of Si and Se are almost equal for the two samples, but the concentrations of S are significantly different and match well the concentrations of observed defect. These results suggest that the observed electron trap is a DX center caused by sulfur. Our attribution of the traps to the sulfur-related DX center can be reinforced from our experience the extensive baking of growth solution is crucial to reducing the concentration of the observed defect. There are many reports which support our attribution indirectly. Krynicki et al. have recently clarified that the observed electron trap is a real DX center.[9] It is also confirmed that the observed trap is not related to oxygen.[20] Moreover, the suppression of the PPC effect in Si- or Se-doped $In_{0.5}Ga_{0.5}P$[12] and Si-doped $In_{0.3}Ga_{0.7}P$[13] has been reported. All these facts, with our results, indicate that the most probable origin of the observed electron trap is a sulfur-related DX center. The fact that the sulfur concentrations in Table 2 are always higher than the defect concentrations in Table 1 can support partly the arguments of Krynicki et al. that the defects are partially ionized at the temperature at which they are detected if the free-carrier concentration is not very high.

IV. CONCLUSIONS

We have observed that only one type of deep electron trap, whose activation energy is about 0.27 eV, irrespective of the Ga composition, exists in LPE-grown undoped n-$In_{0.5}Ga_{0.5}P$ and n-$In_{0.3}Ga_{0.7}P$. The characteristic features of the traps, the dependence of the DLTS spectra on the refilling pulse-time and on the electric-field magnitude, and the alloy broadening phenomena indicate that the traps in the two materials are identical.

From the dependence of the physical properties of the deep levels on the Ga composition in $In_{1-x}Ga_xP$ and the PPC effect observed in some samples of $In_{0.3}Ga_{0.7}P$, we attribute the origin of the observed traps to a DX center caused by an unintentionally doped impurity element. The SIMS results indicate that the most probable origin of the DX center is sulfur.

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