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P. KAMIŃSKI, W. STRUPIŃSKI
INSTYTUT TECHNOLOGII MATERIAŁÓW ELEKTRONICZNYCH
ul. Wólczyńska 133, 01-919 Warszawa

DEEP LEVEL STUDIES IN GaP:N,S EPITAXIAL LAYERS

GaP epitaxial layers doped with nitrogen and sulfur are used for manufacturing electroluminescent devices emitting yellow-green light. The main problem in obtaining high electroluminescent conversion efficiency is to control the concentration of point defects which can act as non-radiative recombination centres. In this paper DLTS technique was applied to investigate the residual deep-level defects in VPE GaP:N,S. Three defect centres with activation energies for electron thermal emission of 0.24 eV, 0.28 eV and 0.44 eV were detected. The concentration of the 0.24-eV and 0.44-eV traps was found to be dependent on substrate temperature. Experimental evidence is given that the 0.24-eV-trap, related to phosphorus vacancy, has a detrimental effect on radiative recombination efficiency in the epitaxial layers.

I. INTRODUCTION

Vapour Phase Epitaxy (VPE) is widely used for growing thin layers of the III-V compound semiconductors which are applied in optoelectronics for the fabrication of Light-Emitting Diodes (LEDs) and displays. Epitaxial gallium phosphide doped with nitrogen and sulfur is a starting material for efficient sources of green or yellow-green light. Nitrogen is an isoelectronic impurity in GaP and it acts as the efficient radiative recombination centre. The radiation is generated due to the decay of excitons bound to nitrogen atoms [1]. The concentration of sulfur determines the Fermi level position.

The radiative recombination of excess charge carriers is, however, accompanied by the nonradiative recombination resulting from deep defect centres which are mainly related to the point defects generated during the growth of the epitaxial layer. These defects have not been established yet, though there are some experimental data [2-4] showing that the nonradiative recombination centres can be attributed to Ga vacancies, deep impurities such as Cu or Fe and complexes: V_{Ga}-O_P, $(V_{Ga})_2$-P_{Ga}, C_{Ga}-O_P and Si_{Ga}-O_P. Stringfellow and Hall [5] have shown that luminescent properties of VPE GaP can be strongly affected by a change in the ratio of $[A^{III}]/[B^{V}]$ where $[A^{III}]$ is the group III component concentration and $[B^{V}]$ is the group V component concentration in the gas phase. They have found that the minority carrier lifetime obtained from the photoluminescent decay measurements increases from 10 to 100 ns with increasing

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the ratio of the partial pressures in the input gas stream $P^o_{HCl}/P^o_{PH_3}$ from 0.3 to 10. This result, obtained for the growth temperature of 840°C, was correlated with the improvement of the LEDs output. Stringfellow and Hall [5], however, have not monitored the changes in the material defect structure and it is not clear whether the improvement of quantum efficiency was due to a diminution of the V_{Ga} concentration or due to an increse in the nitrogen concentration.

In the present work, we employed Deep Level Transient Spectroscopy (DLTS) to monitor a change in the defect structure of VPE GaP:N,S resulting from an increase of substrate temperature in the range of 833 - 858°C. The effect of the change in the point defect concentration on the luminescent properties of the epitaxial layers was also studied.

II. EXPERIMENTAL PROCEDURE

A. Growth Conditions

The epitaxial layers of GaP:N,S were grown on the GaP substrates by hydride VPE method. The growth was held in a vertical RF-heated reactor using the PH_3-HCl-Ga-H_2 system. The layers were doped by addition of NH_3 and H_2S to the vapour phase.
The initial vapour composition was characterized by the following partial pressures:

$P^o_{H_2}$ = 0.94 atm, $P^o_{PH_3}$ = 0.006 atm, P^o_{HCl} = 0.034 atm, $P^o_{H_2S} = 2 \times 10^{-7}$ atm,

$P^o_{NH_3}$ = 0.02 atm.

At the substrate temperatures within the range of 833-858°C, the growth rate was nearly constant and equal to 0.3 μm/min. The typical thickness of the layers was about 30 μm. The depth of the nitrogen doped part was 10 μm.

The GaP substrates were grown by Liquid Encapsulated Czochralski (LEC) technique in the high-pressure crystal-pulling furnace. The substrates were oriented 4° to 7° off the (100) plane towards ⟨100⟩. The electron concentration in the substrate wafers was 2×10^{18} cm^{-3}. Prior to deposition the substrates were in situ etched in HCl at a temperature of 850°C. The substrate temperature was controlled to ±1°C by means of Pt/PtRh thermocouple and optical pyrometer.

B. Sample preparation and testing

The measurements of both electron and deep-level defect concentration were carried out using Schottky-barrier diodes as well as diodes with p^+-n junctions made by Zn diffusion. At least 10 diodes of each kind fabricated from the same epitaxial layer, grown at a given substrate temperature, were measured. Schottky barriers were formed on the epitaxial surfaces by evaporating a thin layer of Au through a mask with a 400 μm - side square opening. The Zn diffusion was carried out in an open tube at a temperature of 650°C for 22 h using a ZnO layer as the source of Zn and an SiO_2 layer as the encapsulant. The typical junction depth was 5 μm. Ohmic contacts were formed by evaporating a thin layer of Au + 1% Si on the n-type substrate surface and an array

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of small Al dots on the p-type surface of the epitaxial layer. The wafer was cleaved into chips which were mounted on TO-18 transistor headers to measure junction characteristics, luminescent properties and DLTS spectra.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. DLTS spectra

The capacitance transient technique used in DLTS is based on the fact that the emission of a carrier from a deep level state is a thermally activated process characterized (for electron emission to the conduction band) by the equation [6]:

$$\tau^{-1} = e_n = \gamma_n \sigma_{na} T^2 \exp(-E_{na}/kT) \tag{1}$$

where τ is the time constant of the process and e_n is, therefore, the emission rate of electrons. E_{na} is the activation energy of electron emission, σ_{na} is the apparent capture cross-section for electrons, k is the Boltzmann constant, T is the absolute temperature and γ_n is the material constant dependent on the effective mass (for GaP $\gamma_n = 9.8\ cm^2 s^{-1} K^{-2}$).

If the capture process is accompanied by multiphonon emission then the electron capture cross-section σ_n, the apparent capture cross-section σ_{na} and the activation energy can be expressed by [6].

$$\sigma_n(T) = \sigma_{n\infty} \exp(-E_\sigma/kT), \tag{2}$$

$$\sigma_{na} = g_n \sigma_{n\infty} \exp(\Delta S_n), \tag{3}$$

$$E_{na} = E_{T0} + E_\sigma , \tag{4}$$

where E_σ is the activation energy for electron capture, $\sigma_{n\infty}$ is the limiting value of σ_n at $T \to \infty$, g_n is the degeneracy factor, ΔS_n is the entropy of the electron transition and E_{T0} is the ionisation energy extrapolated for $T \to 0$ (Gibbs free energy of the transition).

In the DLTS technique the reverse bias applied to a Schottky barier or asymmetrical junction diode is periodically pulsed to zero at a frequency f. After the reverse bias returns, those majority carriers that were captured when the depletion region collapsed will be emitted at a rate dependent upon the temperature and the energy level of the defect, according to eq. (1). The out-of-equilibrium capacitance is related to the time t by the equation [7]

$$\Delta C^* = \Delta C(t_c) \exp(-e_n t), \tag{5}$$

where t_c is the filling pulse width and $\Delta C(t_c)$ is the transient amplitude. Simple DLTS theory predicts [7] that the capacitance transient amplitude as a function of the filling pulse width is given by the following equation

$$\Delta C(t_c) = \Delta C(\infty)[1 - \exp(-t_c/\tau_1)], \tag{6}$$

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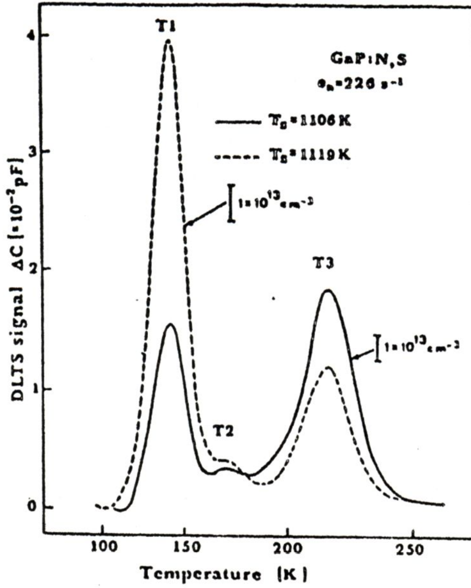

Fig. 1. DLTS spectra for epitaxial layers of GaP:N,S grown at different substrate temperatures

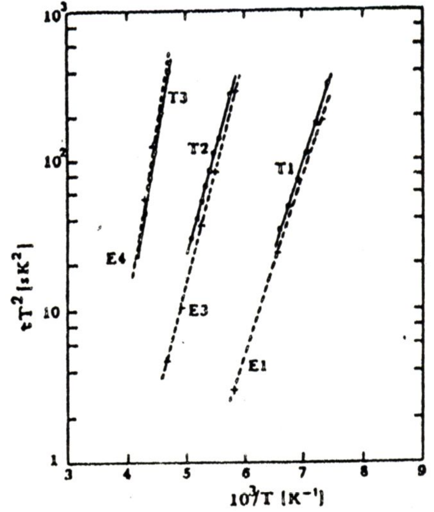

Fig. 2. Arrhenius plots for deep-level defects in VPE GaP:N,S
Broken lines are the signatures of defects reported in [8]

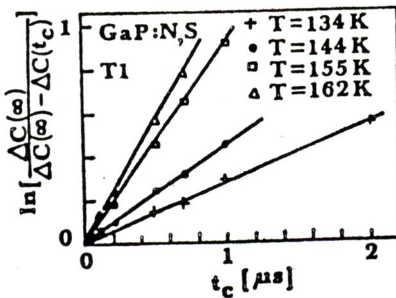

Fig. 3. Changes in the DLTS peak height versus the filling pulse width for the deep-level defect T1.
The solid lines are least-squares fits to the data measured at various temperatures.

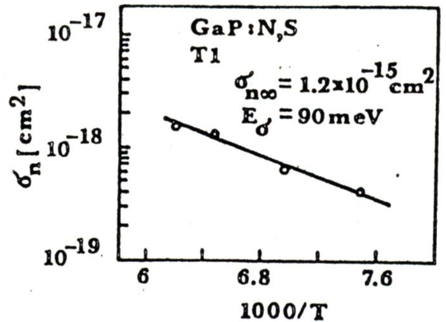

Fig. 4. Temperature dependence of electron capture cross-section for the deep-level defect T1. The activarion energy for electron capture and the value of σ_n for $T \to \infty$ are given

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where $\Delta C(\infty) = \Delta C(t_c \to \infty)$, $\tau_1^{-1} = \sigma_n \langle v_n \rangle n + e_n$, $\langle v_n \rangle$ is the average thermal velocity of electrons and n is the free electron concentration.

The DLTS spectra typical of the epitaxial layers of GaP:N,S grown at two different temperatures are shown in Fig. 1. The spectra were taken using a standard transient capacitance spectrometer DLS-81 at a reverse bias V_R = -4V, a filling pulse amplitude V_F = 3V and a filling pulse width t_c = 100 μs. In all samples three electron traps labelled as T1, T2 and T3 are observed. Moreover, the substrate temperature during the VPE growth has a different effect on the peak height of the two main traps T1 and T2. All the traps were characterized by drawing the Arrhenius plots of log (τT^2), versus 1/T which are shown in Fig. 2. The values of thermal emission activation energy and apparent electron capture cross-section were obtained from least-squares fits to the data according to eq. (1). The Arrhenius plots for the traps T1, T2 and T3 are compared with those reported by Tell and Kuijpers [8]. As can be seen in Fig. 2, they observed the same defect centres labelled E1, E3 and E4. However, they made no suggestion on the atomic configuration of these defects. The parameters of deep-level defects detected in VPE GaP:N,S are listed in Table 1.

Table 1.
Activation energy and apparent electron capture cross-section for deep-level defects in VPE GaP:N,S

Defect	E_{na} (eV)	$E_{na}^{*)}$ (eV)	σ_{na} (cm^2)
T1	0.24 ±0.01	0.23 (E1)	3×10^{-15}
T2	0.28 ±0.01	0.29 (E3)	5×10^{-16}
T3	0.44 ±0.02	0.47 (E4)	7×10^{-14}

*) The values reported by Tell and Kuijpers [8]

According to eq. (1) and (3) the value of σ_{na} obtained by extrapolation of the Arrhenius plots of τT^2 vs 1/T does not represent the accurate determination of σ_n. However, as it is seen from eq. (5) and (6), the capture cross-section can be measured separately by changing the duration of the filling pulse. This procedure was applied to the defect centre T1 and the results obtained are shown in Fig. 3.
The straight lines in Fig. 3 indicate that the capture process for the defect level T1 is of exponential character. The time constant τ_1 was calculated for the different temperatures from the slope of the lines and the temperature dependence of the electron capture cross-section was determined using the known carrier concentration ($n = 5 \times 10^{16} cm^{-3}$). The variations of σ_n as a function of temperature are illustrated in Fig. 4.
A least squares fit to the data according to eq. (2) gave E_σ = (90 ±10) meV and from the extrapolation for $T \to \infty$ we obtained $\sigma_{n\infty} = 1.2 \times 10^{-15} cm^2$. By taking into account eq. (4), the ionisation energy of the defect level T1 was found to be E_{T0} = 0.15 eV.

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The results obtained from the investigation of capture process for the centre T1 are in good agreement with a quantitative theory of nonradiative capture by multi-phonon emission (MPE) developed by Henry and Lang [9]. The theory predicts that the capture cross-sections will increase exponentially with temperature and the capture cross-sections have a common limit σ_∞ between 10^{-15} and 10^{-14} cm^2 when extrapolated to high temperatures. Because of the large electron capture cross-section, the centre T1 is likely to be an effective nonradiative recombination centre in VPE GaP.

B. Models for T1 and T3 centres

The trap T3 has been extensively studied by other investigators [10] who attempted to correlate its concentration with donor and nitrogen doping levels. A significant contribution to the understanding of the microscopic structure of the trap T3 has been made by Ferenczi et al. [11] who found an empirical formula relating the concentration of trap T3 to the electron and nitrogen concentration:

$$N_{T3} = k_1 n \, [N_P]^2, \qquad (7)$$

where k_1 is a constant and $[N_P]$ is the nitrogen concentration. Moreover, the trap T3 was suggested to be a nitrogen split interstitial pair on phosphorus site [11].

Figure 5 shows how the concentration of defects T1 and T3 varies with the substrate temperature. The concentrations of the deep traps are proportional to the heights of the DLTS peaks and were found by means of well-known Lang's method [7]. It is seen that the T1-centre concentration strongly increases with increasing substrate temperature, while there is the opposite effect of the substrate temperature on the T3-centre concentration. In order to explain these experimental results we calculated the Ga- and P-vacancy concentrations. The calculations were performed using the following relationships [2]:

$$[V_{Ga}] = 4.85 \times 10^{-5}(P_{P_2})^{1/2} T \exp(-11920T - 2.62 \times 10^{-5}T), \qquad (8)$$

$$[V_P] = \left\{4.78 \times 10^{8}/(P_{P_2})^{1/2} T\right\} \exp(-32650/T + 2.62 \times 10^{-5}T), \qquad (9)$$

where $[V_{Ga}]$ and $[V_P]$ are the Ga- and P-vacancy concentrations in site fraction units, respectively, and P_{P_2} is the partial pressure of P_2 molecules over GaP. It should be noted that the model [2] which we have used for the evaluation of $[V_{Ga}]$ and $[V_P]$ assumes the Schottky mechanism for vacancy formation. It is also based on the fact that the P_2 molecules, created due to decomposition of PH_3, are the predominant phosphorus source in the gas phase [12]. The value of P_{P_2} was estimated to be 3.9×10^{-3} atm.

Figure 6 shows the T1-centre concentration plotted against calculated $[V_P]$. The straight line was fitted by the least squares method and the nearly linear relationship with the slope of 1.6 and regression coefficient of 0.99 was found. Thus, we can attribute the trap T1 to P vacancy. The main advantage of deep level transient

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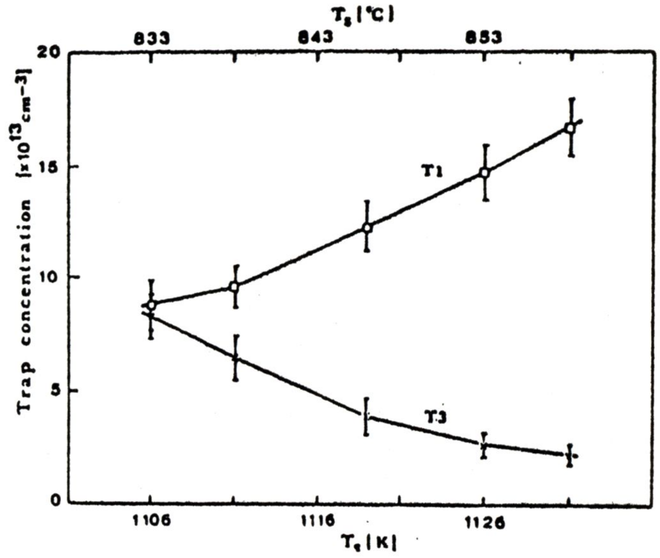

Fig. 5. Variations of the T1- and T3-centre concentrations as a function of substrate temperature

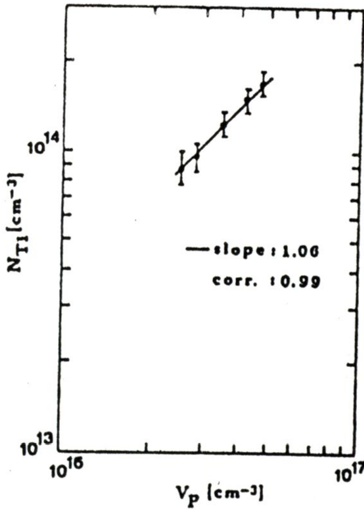

Fig. 6. Dependence of the T1-centre concentration on the calculated P-vacancy concentration. The line is a least squares fit to the data

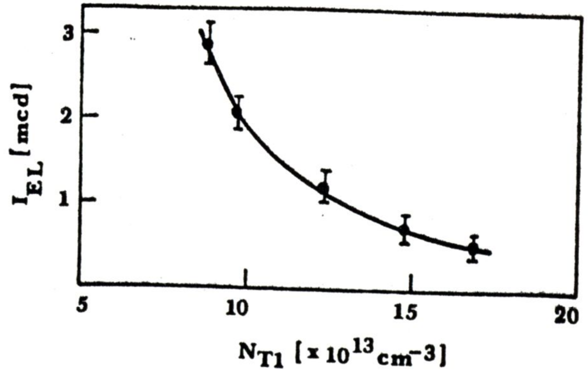

Fig. 7. Variation of the luminous intensity of VPE GaP:N,S light emitting diodes as a function of the T1-centre concentration

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spectroscopy is that it enables one to correlate the quantum efficiency of LEDs with the presence of deep defect centres. The relationship between the luminous intensity of the LEDs fabricated from the epitaxial layers grown at various substrate temperatures and the T1-centre concentration is shown in Fig. 7. This relationship confirms our previous suggestions made on the grounds of the capture process studies and it is clearly seen that the defect centre T1 has a detrimental effect on the radiative recombination efficiency in VPE GaP. In the light of the fact that the trap T1 is related to P vacancy, the results in Fig. 7 give the evidence, that P vacancies, similarly as Ga vacancies, are efficient nonradiative recombination centres.

CONCLUSIONS

DLTS measurements were performed on VPE GaP:N,S LEDs and Schottky barriers fabricated from the epitaxial layers grown at various substrate temperature. In all samples we found three trap levels in the upper half of the forbidden gap:T1 (0.24eV). T2 (0.28eV) and T3 (0.44eV).

The capture process for the trap T1 was studied. The activation energy for electron capture and the limiting value of electron capture cross-section were found to be E_{σ} = 90meV and $\sigma_{n\infty} = 1.2 \times 10^{-15}$ cm^2, respectively. These results are consistent with those predicted by a theory of MPE capture.

A correlation between the T1-centre concentration and the calculated P-vacancy concentration as a function of substrate temperature has been found. The experimental evidence is given that the defect centre T1 has a detrimental effect on the luminescent properties of VPE GaP:N,S.

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