1982

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Repository Citation

Yu, P. W., Mithel, W. C., Mier, M. G., Li, S. S., & Wang, W. (1982). Evidence of Intrinsic Double Acceptor in GaAs. *Applied Physics Letters, 41* (6), 532-534.
https://corescholar.libraries.wright.edu/math/28

Evidence of intrinsic double acceptor in GaAs

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(Received 2 June 1982; accepted for publication 29 June 1982)

Acceptors present in undoped *p*-type conducting GaAs have been studied with photoluminescence, temperature-dependent Hall measurements, deep level transient spectroscopy, and spark source mass spectrometry. It is shown that *p*-type conduction is due to presence of the shallow acceptor C_{As} and the cation antisite double acceptor $\mathrm{Ga}_{\mathrm{As}}$. The first and second ionization energies determined for $\mathrm{Ga}_{\mathrm{As}}$ are 77 and 230 meV from the valence-band edge.

PACS numbers: 71.55.Fr, 78.55.Ds, 72.80.Ey

GaAs has been of great interest both because of its technological importance and its fundamental properties. The role of deep impurities and intrinsic defects as electrically active centers has long been known in GaAs. Recently, many studies have been made of intrinsic vacancies and antisite defects, formed due to stoichiometry deviation during crystal growth[1] and electron or neutron irradiation. In particular, several works[2–4] show that the anion antisite $\mathrm{As}_{\mathrm{Ga}}$ is responsible for a main electron trap located at ~0.75 eV from the conduction band (commonly known as EL2).

Recently, we have identified[5,6] an acceptor level located at 77 meV from the valence-band edge present in liquid encapsulated Czochralski (LEC) grown materials. The acceptor is present both in *p*-type conducting and *n*-type semi-insulating crystals grown from Ga-rich melts. The 77-meV acceptor was attributed to a center involving a cation antisite double acceptor $\mathrm{Ga}_{\mathrm{As}}$ on the basis of the background impurities, crystal growth in Ga-rich melts, and the presence of near-intrinsic emissions corresponding to antisite defects.[7] In this letter we present the result of studies on acceptors present in undoped bulk *p*-type materials. The experimental methods employed are photoluminescence (PL), temperature-dependent Hall measurements (TDH), deep level transient spectroscopy (DLTS), and spark source mass spectrometry (SSMS). The results show that all observed acceptors including the 77-meV acceptor can be attributed to the presence of C_{As} and the double acceptor $\mathrm{Ga}_{\mathrm{As}}$.

TABLE I. Detailed physical parameters obtained with four different experimental techniques (energy in meV and concentration in cm^{-3}).

Sample	Method	Parameters	C_{As}	$\mathrm{Ga}_{\mathrm{As}}^{0}/\mathrm{Ga}_{\mathrm{As}}^{-}$	$\mathrm{Ga}_{\mathrm{As}}^{-}/\mathrm{Ga}_{\mathrm{As}}^{2-}$
A	SSMS	C	$\lesssim 4\times10^{15}$ (Total)		
	PL	E_{Ai}	26	77	230
	DLTS	E_{Ai}		80	
		N_T		4.1×10^{15}	
	Hall	E_{Ai}	23	71	199
		N_{Ai}	5.8×10^{15}	7.0×10^{15} (Total $\mathrm{Ga}_{\mathrm{As}}$)	
		N_D		1.0×10^{15} (Total donor)	
B	SSMS	C	4×10^{15} (Total)		
	PL	E_{Ai}	26	77	230
	DLTS	E_{Ai}		80	
		N_T		2.4×10^{16}	
	Hall	E_{Ai}	23	66	
		N_{Ai}	9.7×10^{15}	4.4×10^{16} (Total $\mathrm{Ga}_{\mathrm{As}}$)	
		N_D		7.3×10^{15} (Total donor)	

Two wafers of *p*-type conducting crystals grown by LEC method were chosen for this study. PL excitation was made with a 647.1-nm line of a Kr laser with a maximum intensity of ~400 mW. A van der Pauw configuration was employed for TDH measurements. Ohmic contacts were made by evaporation of Ag-Mn alloy and an Al-Schottky barrier structure was used for DLTS and capacitance-voltage (C-V) measurements. SSMS was performed with liquid-helium cryopumping in the source region and 170 °C bakeout processing before analysis in order to reduce the background impurities such as C and O.

SSMS shows that the main background impurities are C and B. The concentration of B for sample A is 4×10^{16} cm^{-3} whereas sample B shows a surface contamination in the range 4×10^{15}–4×10^{16} cm^{-3}. The concentration of C is listed in Table I. Other impurities are not our concern simply because the concentration is much less than 4×10^{15} cm^{-3}.

Figure 1 shows the $T = 4.2$-K PL characteristics obtained from sample A. The spectrum consists of the near-intrinsic region emissions at ~1.51 eV, the neutral donor-acceptor pair (D^0-A^0) and the free-electron-bound hole at neutral acceptor (e-A^0) transition involving C_{As} at ~1.493 eV, the 1.441-eV emission due to the 77-meV acceptor, and a very weak emission at 1.284 eV with its LO phonon. Sample B shows the same emission characteristics as sample A. However, the relative intensity of the 1.441 eV vs 1.493-eV emission is larger for sample B. Temperature dependence of the 1.441-eV emission in the two samples yields the same

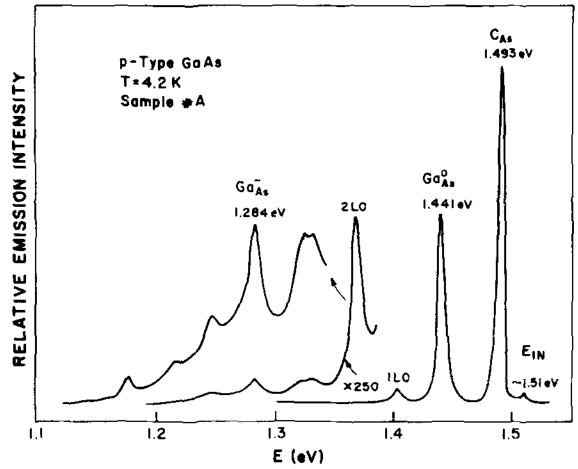

FIG. 1. $T = 4.2$-K PL characteristics of a p-type sample (sample A). The near-intrinsic region emission ($E_{\rm In}$), C$_{\rm As}$-related emission at 1.493 eV and the emissions at 1.441 and 1.284 eV due to Ga$^0_{\rm As}$ and Ga$^-_{\rm As}$, respectively, are seen.

acceptor activation energy of 77 ± 2 meV as determined in the previous work.[5] The peak energy of the 1.441-eV emission in the form of the (e-A^0) transition follows Eagles' expression[8] for the (e-A^0) transition. Thus, the temperature dependence of the acceptor is negligible.

Figure 2 shows a DLTS scan of hole trap for sample A. Sample B also shows the same DLTS scan. Namely, one major hole trap is observed within our experimental range. The apparent activation energy was obtained by the usual relation[9,10] of the hole emission rate e_p/T^2 vs $1/T$. The temperature correction for the hole capture cross section was made by the capture cross-section σ_p vs $1/T$ relation. The obtained value of the apparent activation energy is 130 meV from the valence band. The activation energy of the major hole trap is 80 meV after the temperature correction of 50 meV of capture cross section (the obtained value of $\sigma_{p\infty}$ is 7.1×10^{-15} cm^2). Therefore, it is evident that this trap at 80 meV is the same center observed as the 1.441-eV emission under photoexcitation. The density of the hole trap determined[9,10] by $N_T = (N_A - N_D)2\Delta C/C$ under a complete filling condition is given in Table I.

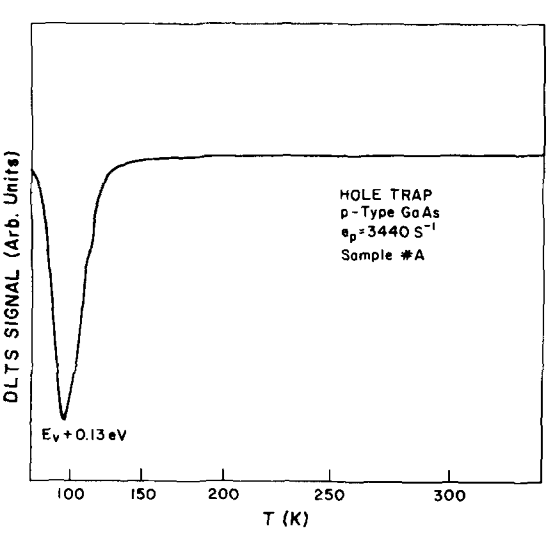

FIG. 2. DLTS scan of hole traps in a p-type sample (sample A).

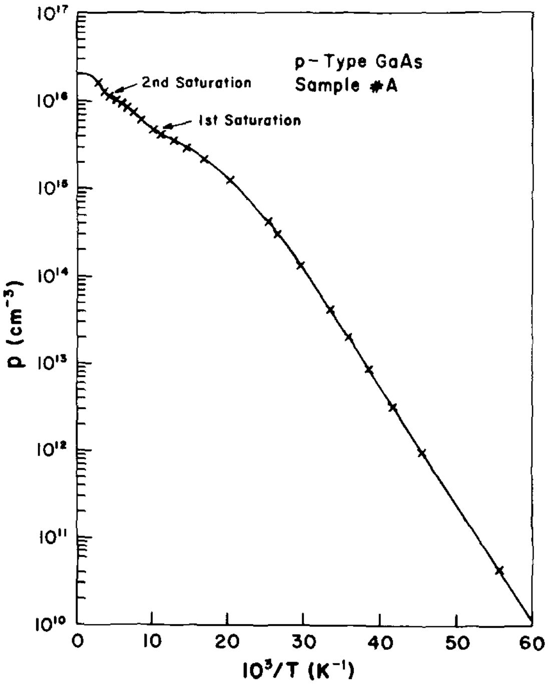

FIG. 3. Hole concentration p vs $10^3/T$ for a p-type sample (sample A).

Hole concentration p vs $1/T$ relation obtained from sample A is shown in Fig. 3 (similar Hall data were presented by other workers elsewhere).[11,12] Hole concentration was calculated with the Hall factor being unity. Figure 3 shows two saturation regions in p vs $1/T$ relation. This indicates the presence of three acceptor levels. However, sample B shows only one saturation in the temperature range of our measurements due to a higher concentration of second acceptor.

Now, let us consider the nature of the antisite double acceptor Ga$_{\rm As}$. Recent calculation by Louis and Vergés[13] shows that possible bound states of antisite defects in GaAs are A_1 and T_2 states. The T_2 state has threefold orbital degeneracy and twofold spin degeneracy. In particular, the neutral state of Ga$_{\rm As}$ is the T_2 state occupied by four electrons. Therefore, neutral, singly, and doubly charged states (Ga$^0_{\rm As}$, Ga$^-_{\rm As}$, and Ga$^{2-}_{\rm As}$) can exist for Ga$_{\rm As}$. Following the usual notation we call the degeneracy factors corresponding to Ga$^0_{\rm As}$, G$^-_{\rm As}$, and Ga$^{2-}_{\rm As}$ state respectively $g_{\rm Ga0}$, $g_{\rm Ga1}$, and $g_{\rm Ga2}$. The value of degeneracy factors depends on the splitting of the T_2 state due to Jahn–Teller distortion. However, no splitting of the T_2 state is likely with the expectation[13] of a very weak Jahn–Teller distortion as in the case of the effective-mass acceptors. The values of $g_{\rm Ga0}$, $g_{\rm Ga1}$, and $g_{\rm Ga2}$ are 15, 6, and 1 under no splitting of the T_2 state, respectively.

We analyze the Hall data with two acceptors C$_{\rm As}$ and Ga$_{\rm As}$. A charge neutrality condition for p-type sample can be given[14] as follows:

$$p + N_D = N^-_{\rm C} + N^-_{\rm Ga} + 2N^{2-}_{\rm Ga}, \tag{1}$$

$$N^-_{\rm C} = \frac{N_{\rm C}}{(1 + g_{\rm C0}/g_{\rm C1})(p/N_v)\exp(E_{\rm C}/kT)}, \tag{2}$$

$$N^-_{\rm Ga} = N_{\rm Ga}\left[1 + \frac{g_{\rm Ga0}}{g_{\rm Ga1}}\frac{p}{N_v}\exp\left(\frac{E_{\rm Ga1}}{kT}\right)\right.$$

$$+\frac{g_{\mathrm{Ga2}}}{g_{\mathrm{Ga1}}}\frac{N_v}{p}\exp\left(-\frac{E_{\mathrm{Ga2}}}{kT}\right)\Bigg]^{-1}, \tag{3}$$

$$N_{\mathrm{Ga}}^{2-}=N_{\mathrm{Ga}}\Bigg[1+\frac{g_{\mathrm{Ga0}}}{g_{\mathrm{Ga2}}}\left(\frac{p}{N_v}\right)^2\exp\left(\frac{E_{\mathrm{Ga1}}+E_{\mathrm{Ga2}}}{kT}\right)$$
$$+\frac{g_{\mathrm{Ga1}}}{g_{\mathrm{Ga2}}}\frac{p}{N_v}\exp\left(\frac{E_{\mathrm{Ga2}}}{kT}\right)\Bigg]^{-1}, \tag{4}$$

where N_{C} is the total C_{As} acceptors, N_{Ga} is the total number of $\mathrm{Ga}_{\mathrm{As}}$, N_v is the density of state in the valence band, and N_D is the total donors. E_{C}, $\mathrm{E}_{\mathrm{Ga1}}$, and E_{Ga2} are the activation energies attributable to C_{As}, $\mathrm{Ga}_{\mathrm{As}}^0/\mathrm{Ga}_{\mathrm{As}}^-$, and $\mathrm{Ga}_{\mathrm{As}}^-/\mathrm{Ga}_{\mathrm{As}}^{2-}$, respectively. $\mathrm{Ga}_{\mathrm{As}}^0/\mathrm{Ga}_{\mathrm{As}}^-$ and $\mathrm{Ga}_{\mathrm{As}}^-/\mathrm{Ga}_{\mathrm{As}}^{2-}$ mean the first and second ionization states of the double acceptor $\mathrm{Ga}_{\mathrm{As}}$. However, as a good approximation of Eq. (1) we use the following equation:

$$p+N_D=N_{\mathrm{C}}^-+\frac{N_{\mathrm{Ga}}}{(1+g_{\mathrm{Ga0}}/g_{\mathrm{Ga1}})(p/N_v)\exp(E_{\mathrm{Ga1}}/kT)}$$
$$+\frac{2N_{\mathrm{Ga}}}{(1+g_{\mathrm{Ga1}}/g_{\mathrm{Ga2}})(p/N_v)\exp(E_{\mathrm{Ga2}}/kT)}. \tag{5}$$

The solid line in Fig. 3 is obtained by the least-square fit with the degeneracy factors $g_{\mathrm{Ga's}}$ under no splitting of the T_2 state. The degeneracy factors for C_{As}, g_{C0} and g_{C1} are, respectively, 4 and 1. The value used for N_v is $1.7\times10^{15}\,T^{3/2}$. The activation energies are 23, 71, and 199 meV, which can be attributable to C_{As}, $\mathrm{Ga}_{\mathrm{As}}^0/\mathrm{Ga}_{\mathrm{As}}^-$, and $\mathrm{Ga}_{\mathrm{As}}^-/\mathrm{Ga}_{\mathrm{As}}^{2-}$. For example B Hall data were analyzed with two acceptor levels due to C_{As} and $\mathrm{Ga}_{\mathrm{As}}^0/\mathrm{Ga}_{\mathrm{As}}^-$.

Table I shows the results of our experiment. First, C_{As} is a major shallow acceptor. The concentration of C determined by SSMS agrees within a factor of 2 with that determined by Hall measurements. Second, the values determined for the second acceptor level are consistent considering the different experimental techniques employed. As discussed in the previous work,[5] B can be a double acceptor by sitting in As sites. However, the local mode spectroscopy shows[15] that B is mostly substitutional in Ga sites and that B_{As} does not occur in p-type material. Also, the concentration of $\mathrm{Ga}_{\mathrm{As}}$ does not support any direct association of B with the 77-meV acceptor. Other impurities are less than 4×10^{15} cm^{-3}. Therefore, it is clear that impurity or impurity association is not involved in the 77-meV acceptor. Third, the presence of the third level from Hall data is clear even though higher temperatures are needed to observe third saturation range. We also note that PL spectrum in Fig. 1 shows an emission at 1.284 eV with a very small intensity compared to 1.441-eV emission. The 1.284-eV emission is present with the 1.441-eV emission and can always be correlated in intensity with the 1.441-eV emission. Therefore, the 1.284-eV emission can be attributed to $\mathrm{Ga}_{\mathrm{As}}^-/\mathrm{Ga}_{\mathrm{As}}^{2-}$ state as a form of $(D^0\text{-}A^0)$, $(e\text{-}A^0)$ or the two combination. The second ionization energy is ~230 meV, which is consistent with the value determined by Hall measurements. The smaller intensity is due to the smaller concentration ratio of the singly ionized versus neutral $\mathrm{Ga}_{\mathrm{As}}$ and due to the electron capture of the repulsive center $\mathrm{Ga}_{\mathrm{As}}^-$ under our PL excitation condition. These facts explain well the presence of $\mathrm{Ga}_{\mathrm{As}}^-/\mathrm{Ga}_{\mathrm{As}}^{2-}$ state together in Hall measurements. Naturally, the 1.441-eV emission studied[5] in detail previously is due to $\mathrm{Ga}_{\mathrm{As}}^0/\mathrm{Ga}_{\mathrm{As}}^-$ as the forms of $(D^0\text{-}A^0)$ and $(e\text{-}A^0)$ transitions.

Our explanation of the acceptor levels present in p-type LEC materials is based on the centers C_{As} and $\mathrm{Ga}_{\mathrm{As}}$. The first and second ionization energies of $\mathrm{Ga}_{\mathrm{As}}$ are, respectively, at 77 and 230 meV from the valence band as determined by PL method. We now show that these ionization energies are consistent with other well-known examples of double acceptors. First, let us consider Ge:Zn. We note that these elements are isocoric[16] with Ga and As. Therefore, ionization energies of $\mathrm{Ga}_{\mathrm{As}}$ can be obtained by adjusting the acceptor parameters involved in the acceptor model of Balderish and Lipari.[17] We obtain 86 and 225 meV for $\mathrm{Ga}_{\mathrm{As}}^0/\mathrm{Ga}_{\mathrm{As}}^-$ and $\mathrm{Ga}_{\mathrm{As}}^-/\mathrm{Ga}_{\mathrm{As}}^{2-}$ by using[18,19] 32.6 and 85.8 meV for $\mathrm{Zn}^0/\mathrm{Zn}^-$ and $\mathrm{Zn}^-/\mathrm{Zn}^{2-}$ in Ge, respectively. Similarly, we also obtain 82 and 245 meV for $\mathrm{Ga}_{\mathrm{As}}^0/\mathrm{Ga}_{\mathrm{As}}^-$ and $\mathrm{Ga}_{\mathrm{As}}^-/\mathrm{Ga}_{\mathrm{As}}^{2-}$ using 34 and 102 meV from GaSb intrinsic acceptor levels.[20] Also it is mentioned that other examples of double acceptor can be found in the metal vacancy system[21] in II-VI compounds.

In conclusion, the present work shows that p-type conduction in materials grown under nonstoichiometry condition is well explained by C_{As} and an intrinsic acceptor. The intrinsic acceptor is due to the $\mathrm{Ga}_{\mathrm{As}}$. Therefore, the intrinsic acceptor $\mathrm{Ga}_{\mathrm{As}}$ as well as the intrinsic donor $\mathrm{As}_{\mathrm{Ga}}$ play important roles in compensation mechanism in GaAs as predicted by van Vechten.[22] In practical GaAs technology, this work presents the importance of stoichiometry control during crystal growth.

We would like to thank D. C. Reynolds and D. C. Look for many discussions. The work of P. W. Yu was performed at the Avionics Laboratory, Wright–Patterson AFB under contract No. F33615-81-C-1406. The work of S. S. Li and W. I. Wang is supported by AFOSR Grant No. F33615-79-C-5129.

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