

## INFLUENCE OF ARSENIC VAPOR SPECIES ON ELECTRICAL AND OPTICAL PROPERTIES OF MBE GROWN GaAs

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**Résumé.** - L'influence respective des espèces gazeuses de l'arsenic dimères ( $As_2$ ) et tétramères ( $As_4$ ) sur les propriétés électriques et optiques de GaAs, non dopé et dopé par Ge, élaboré par épitaxie de jet moléculaire (MBE), a été étudiée par effet Hall, photoluminescence (PL) et mesures DLTS. Le jet moléculaire provenait de deux sources  $As_2$  et  $As_4$  différentes ainsi que d'une source unique pouvant fournir des rapports de flux  $As_4/As_2$  réglables. L'apparition de lignes d'exciton de saut reliées au défaut dans le spectre 2K PL est directement corrélée à l'existence de trois états profonds (M1, M3, M4), qui sont caractéristiques de GaAs élaboré par la méthode MBE. L'intensité de ces PL lignes supplémentaires et, simultanément la concentration des électrons piégés peuvent être réduites substantiellement par diminution du rapport de  $As_4$  sur  $As_2$ . De plus, un rapport d'autocompensation beaucoup plus faible dans n-GaAs dopé au Ge peut être obtenu par un jet moléculaire d'espèces  $As_2$ , qui fournit une population de surface de l'arsenic nettement plus stationnaire. Les résultats démontrent que l'incorporation des centres reliés au défaut aussi bien que celle de dopants amphotériques dépend fortement de l'état chimique de la surface impliquée lors du processus de croissance du film.

**Abstract.** - The influence of dimeric ( $As_2$ ) vs tetrameric ( $As_4$ ) arsenic vapour species on the electrical and optical properties of undoped and of Ge-doped GaAs grown by molecular beam epitaxy (MBE) has been studied by using Hall effect, photoluminescence (PL) and DLTS measurements. The arsenic molecular beam was obtained from separate  $As_2$  and  $As_4$  sources, resp., and from a single source providing adjustable  $As_4/As_2$  flux ratios. The occurrence of the defect related bound exciton lines in the 2K PL spectra was found to be directly correlated with the existence of three deep states (M1, M3, M4) which are characteristic of MBE grown GaAs. The intensity of these extra PL lines and simultaneously the electron trap concentration could be reduced substantially by decreasing the  $As_4$  vs  $As_2$  flux ratio. In addition, a considerably lower autocompensation ratio in Ge-doped n-GaAs was achieved with  $As_2$  molecular beam species which provide a much higher steady-state arsenic surface population. These results demonstrate that the incorporation of defect related centers as well as of amphoteric dopants strongly depends on the surface chemistry involved in the film growth process.

1. **Introduction.** - In the growth of GaAs films by molecular beam epitaxy (MBE) the arsenic molecular beam consists of either tetrameric ( $As_4$ ) [1] or dimeric ( $As_2$ ) species [2]. Generally,  $As_4$  molecular beams produced by evaporating polycrystalline arsenic source material are employed. For the more laborious generation of  $As_2$  molecules during MBE, there are now three methods available: (a) the incongruent evaporation of GaAs source material [3], (b) the thermal decomposition of gaseous  $AsH_3$  in a special leak-effusion source [4] or cracking furnace [5], and (c) the cracking of  $As_4$  into  $As_2$  species in a two-zone effusion cell arrangement [6,7].

Previous studies indicated that the quality of MBE GaAs films is probably

superior when grown from dimeric arsenic species [7, 8]. Low-temperature photoluminescence (PL) measurements showed the existence of additional sharp PL lines in the range 1.504 - 1.511 eV which are due to radiative recombination of bound excitons induced by point defects [8]. The occurrence of these defects was correlated with the complex second-order interaction process of the impinging  $As_4$  molecules on the (100) GaAs growth surface [1]. Except for the line at 1.5109 eV, the extra PL features disappeared totally when  $As_2$  instead of  $As_4$  beam species were used, thus indicating a substantial decrease of growth induced defects. A comparable reduction of the concentration of deep electron traps in  $As_2$ -grown MBE GaAs was derived from DLTS measurements [7].

The apparent advantage of  $As_2$  over  $As_4$  species in MBE of GaAs was attributed to the elementary first-order reaction process of dissociative chemisorption of  $As_2$  involving only a single Ga surface atom [2]. This reduces the probability of incorporation of point defects related to Ga vacancies and their descendants [8]. In addition, it has been speculated that a higher steady-state arsenic surface population during growth exists with  $As_2$  beam species. If so, this should also have a strong impact on the incorporation of amphoteric dopants in MBE GaAs.

In this paper we present the results of combined Hall effect, low-temperature PL and DLTS measurements on not intentionally doped and on Ge-doped GaAs layers grown from separate  $As_4$  and  $As_2$  sources, resp., or from a single source providing adjustable  $As_4/As_2$  flux ratios. In addition to the incorporation of defect related centers, we examine the autocompensation ratio and thereby the site occupancy of the amphoteric dopant Ge. The results are then correlated with the different surface chemistry involved with  $As_2$  and  $As_4$  molecular beams.

**2. Experimental.** - The GaAs films were grown in a UHV system of the vertical evaporation type equipped with a sample exchange load-lock device [9]. For the present study we operated four effusion cells to evaporate elemental arsenic, gallium and germanium as well as polycrystalline GaAs. The epitaxial GaAs layers with a thickness of 2  $\mu\text{m}$  were deposited without any buffer layer simultaneously onto (100) oriented Cr-doped Si and heavily Si-doped n-GaAs substrates. During deposition, the substrate temperature was typically maintained at 550  $^\circ\text{C}$ , if not quoted otherwise. The temperatures of the effusion cells containing Ga and elemental arsenic (lower part of the cell only!) or GaAs, resp., were kept constant throughout the growth runs resulting in a constant growth rate of 1.0  $\mu\text{m}/\text{h}$  and a constant arsenic-to-gallium flux ratio of about two, which produces the As-stabilized (2x4) reconstruction on the (100) growth surface. During this study we adjusted the temperature of the Ge effusion cell to yield a constant dopant flux for a free-electron concentration in the grown layers of between  $1 \times 10^{18} \text{ cm}^{-3}$  and  $4 \times 10^{16} \text{ cm}^{-3}$  depending on the autocompensation ratio.

The elemental arsenic was evaporated in a two-zone 20  $\text{cm}^3$  capacity effusion cell made from high-purity quartz glass which has been described in Ref. 10. The two zones could be heated independently and their temperatures measured by W-Re thermocouples were recorded separately. The temperature of the lower (evaporation) zone determines the total flux, while the temperature of the upper (cracking) zone determines the emerging  $As_4/As_2$  ratio. This arrangement made feasible a very efficient cracking of the evaporating tetrameric species into dimeric species, the amount depending only on the temperature of the removable upper zone. The generation of adjustable  $As_4/As_2$  flux ratios from a single source avoids the introduction of any additional impurities from separate  $As_2$  and  $As_4$  sources. Operation of the cracking zone at temperatures below 500  $^\circ\text{C}$  yields a pure  $As_4$  flux, whereas operation of that zone at 850  $^\circ\text{C}$  generates a beam consisting of at least 90%  $As_2$ . The undoped GaAs films grown from the single elemental arsenic source exhibited compensated or slightly n-type behaviour with electron concentrations below  $1 \times 10^{15} \text{ cm}^{-3}$ . Even at 850  $^\circ\text{C}$  cracker temperature there was no measurable influence on the layer quality. After evaluation through 300 K and 77 K Hall effect measurements, the samples were studied by detailed photoluminescence measurements at temperatures below 2 K. Excitation was performed by the 6471 Å line of a Kr<sup>+</sup> laser using a power density of  $1 \text{ W cm}^{-2}$ . The excitation power was adjusted by neutral density filters. The luminescence light was analysed by a grating monochromator with 1 Å resolution and detected by a photon counting system attached to a cooled GaAs photocathode photomultiplier.

The DLTS measurements of layers grown on n<sup>+</sup>-substrates were performed on Au

Schottky barrier diodes using a fully automated measuring system, which has been described elsewhere [11]. During measurement the samples were biased at -2.0 V. The whole capacitance transient was recorded after applying a short voltage puls of 2.0 V to zero-bias the sample. The emission rates of the electron traps were then calculated from the time constant of the capacitance transient. The temperature dependence of the thermal emission rates yielded the activation energy of the traps and allowed a comparison with data from the literature [12]. The trap concentrations were determined directly from the peak height of the DLTS signal, the total capacitance, and the free-electron concentration as determined by Hall measurements.

3. Results and Discussion. -

3.1 Photoluminescence Investigations. - Two typical low-temperature PL spectra of MBE GaAs in the near band gap energy

region are shown in Fig. 1. The upper spectrum was obtained from a nominally undoped GaAs layer grown with the cracking zone of the arsenic effusion cell kept at a temperature of 300 °C. The well-known emission lines of the free exciton, FE, the donor bound-exciton, (D<sup>0</sup>, X), and the acceptor bound-exciton, (A<sup>0</sup>, X), are clearly resolved [13]. In addition, the emission structures at energies below 1.51 eV appear, which have been attributed to defect induced bound excitons [8]. The entire PL spectrum shows thus the same peculiarities as if the sample was grown from a standard one-zone As<sub>4</sub> source, as shown in Fig. 2.

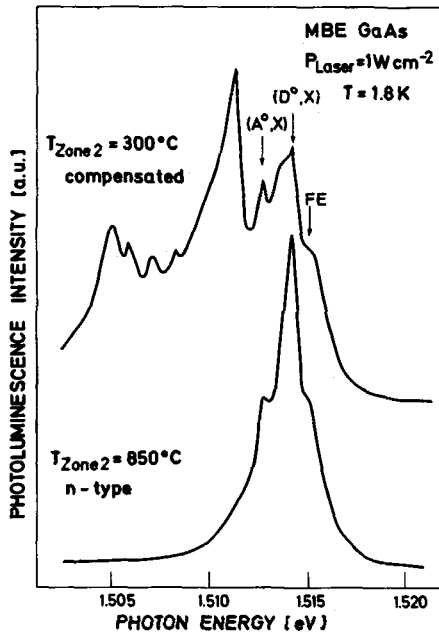


Fig. 1 : Comparison of 1.8 K photoluminescence spectra obtained from nominally undoped MBE GaAs layers grown from predominantly As<sub>4</sub> (top) and As<sub>2</sub> (bottom) molecular beam species of the two-zone effusion cell.

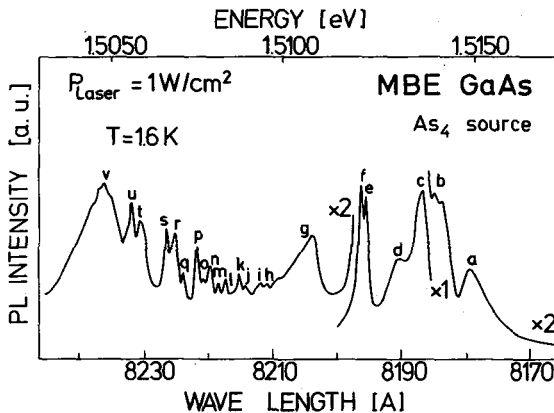


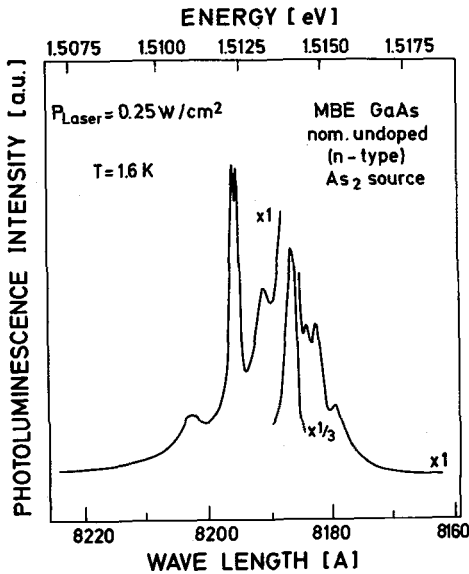
Fig. 2 : Highly resolved 1.6K PL spectrum of a 3 μm thick MBE GaAs layer (p-type) grown from Ga and As<sub>4</sub> species (expanded scale with resolution better than 1 Å).

The assignment of the observed spectral features is displayed in Fig. 3.

When the temperature of the cracking zone of the arsenic effusion cell was stepwise increased, however, the PL intensities of the excitonic structures below 1.51 eV were gradually reduced. Inspection of the lower spectrum in Fig. 1 reveals that

Line	Energy (eV) (±0.1 meV)	Assignment
a	1.5156	free exciton
b	1.5144	excited states of (D <sup>+</sup> ,X)
c	1.5140	exciton bound to neutral donor(D <sup>0</sup> ,X)
d	1.5134	exciton bound to ionized donor(D <sup>+</sup> ,X)
e	1.5124	J=3/2 <sub>1</sub> exciton bound to neutral
f	1.5122	J=5/2 <sub>1</sub> acceptor(A <sup>0</sup> ,X)
g	1.5109	defect induced bound excitons
h	1.5095	
i	1.5093	
j	1.5089	
k	1.5087	
l	1.5084	
m	1.5082	
n	1.5079	
o	1.5077	
p	1.5075	
q	1.5071	
r	1.5069	
s	1.5066	
t	1.5058	
u	1.5056	
v	1.5049	

Fig. 3 : Assignment of 1.6K near band gap emission features of MBE GaAs grown from As<sub>4</sub> species as shown in Fig. 2 (conversion factor is  $E(\text{eV}) = 12395 / \lambda (\text{\AA})$  ).



finally, at a cracker temperature of 850 °C, the defect induced bound exciton lines have completely disappeared, i.e. their intensities are now below the detection limit of our luminescence experiment. This spectrum exhibits the same detailed features as if the sample was grown from pure As<sub>2</sub> generated by incongruent evaporation of GaAs in a separate source (Fig. 4) [8]. The first marked reduction of the intensities of the extra emission lines starts at a temperature of the cracking zone above 700 °C. This indicates that in this temperature regime the As<sub>4</sub>/As<sub>2</sub> flux ratio emerging from the effusion cell changes toward a direction that favours the amount of As<sub>2</sub> species achieving the precursor state before the reaction with the GaAs growth surface.

Fig. 4 : 1.6K PL spectrum obtained from a nominally undoped MBE GaAs layer (n-type) grown from As<sub>2</sub> species (generated by incongruent evaporation of GaAs).

Our results of the PL studies clearly demonstrate that the intensity of the emission due to point defect induced bound excitons decreases continuously with the reduction of the ratio of tetrameric to dimeric arsenic species in the molecular beam. In particular, this result excludes any additional extrinsic impurity from a separate arsenic source which was recently claimed to be responsible for the occurrence of those additional PL structures at energies below 1.51 eV by Scott et al. [14].

3.2 DLTS Investigations. - The results of our DLTS measurements were used to determine directly any correlation between the observed continuous reduction of PL intensity due to defect induced bound excitons and the overall electron trap concentration as a function of decreasing As<sub>4</sub>/As<sub>2</sub> ratio in the arsenic molecular beam. For these studies, the samples were intentionally doped with germanium. Three typical DLTS spectra obtained from MBE grown n-GaAs:Ge layers are shown in Fig. 5. The DLTS signal was normalized for the spectra of all three samples so that one scale is valid for the trap concentration. The lower spectrum of Fig. 5 was taken from a sample (# 1308) grown with the cracking zone of the effusion cell operated at 500 °C. The observed three dominant features labeled M1, M3, and M4 according to Ref. 12

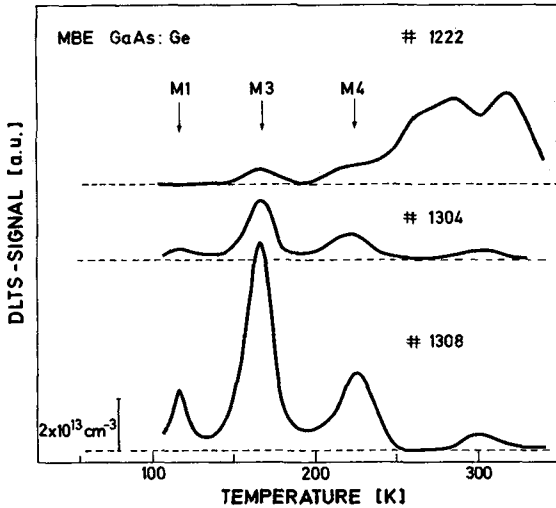


Fig. 5 : DLTS spectra of electron traps in MBE n-GaAs:Ge layers grown with different  $As_2/As_4$  flux ratios. The trap concentration scale is the same for all three samples.

are characteristic for MBE GaAs films grown with As-stabilized (2x4) surface reconstruction. At emission temperatures of 300 K we observed an additional emission structure denoted as M6 electron trap [12]. Inspection of the upper trace in Fig. 5 shows that we could achieve a drastic reduction of the peak heights of the traps M3 and M4, with trap M1 being below the detection limit, when we used pure  $As_2$  instead of  $As_4$  species from a GaAs source during MBE growth. In addition, an unresolved superposition of several trap signals in the region of the M5, M6 and M7 traps appears, which was also observed by Lang et al. [12]. Since these features are not sensitive to the applied  $As_4/As_2$  ratio and differ from sample to sample, we considered only the most important traps M1, M3 and M4 for a further systematic study.

Detailed trap concentrations of four MBE n-GaAs:Ge samples grown with different  $As_4/As_2$  ratios in the arsenic molecular beam are summarized in Table 1. We observed

Table 1. Concentration of M1, M3 and M4 deep levels in MBE n-GaAs:Ge layers with different  $As_2/As_4$  molecular beam flux ratios indicated by the temperature ( $T_{Zone\ 2}$ ) of the cracking zone

MBE GaAs:Ge	$N_D - N_A$ [ $cm^{-3}$ ]	$T_{Zone\ 2}$ [°C]	$N_I^{M1}$ [ $cm^{-3}$ ]	$N_I^{M3}$ [ $cm^{-3}$ ]	$N_I^{M4}$ [ $cm^{-3}$ ]	$\Sigma N_I / (N_D - N_A)$
# 1308	$2.2 \times 10^{16}$	500	$2.2 \times 10^{13}$	$7.5 \times 10^{13}$	$2.9 \times 10^{13}$	0.57%
# 1304	$1.9 \times 10^{16}$	700	$8.4 \times 10^{12}$	$2.3 \times 10^{13}$	$1.2 \times 10^{13}$	0.24%
# 1310	$3.7 \times 10^{16}$	800	-	$3.4 \times 10^{13}$	$2.9 \times 10^{13}$	0.17%
# 1222	$3.0 \times 10^{16}$	pure $As_2$	-	$1.3 \times 10^{13}$	$1.8 \times 10^{13}$	0.10%

a considerable decrease of the overall concentration of M1, M3, and M4 traps relative to the free-carrier concentration, when we reduced the tetrameric-to-dimeric ratio of arsenic species by increasing the temperature of the cracking zone. More than a fivefold reduction in trap concentration (M1, M3, M4) was achieved by this procedure. This value could be further reduced to below  $10^{-3}$  of the free-carrier concentration by increasing the substrate temperature to 580 °C.

3.3 Investigation of Incorporation. - Next, we performed a more detailed examination of the arsenic surface population during growth by considering the incorporation of Ge impurities. The group-IV-element Ge is an amphoteric dopant in MBE GaAs.

It has been shown previously [15, 16] that the Ge incorporation depends critically on the Ga and As sites available on the growing GaAs surface, i.e. on the applied  $As_4/Ga$  flux ratio and on the substrate temperature. Therefore, the measurable ratio of autocompensation  $[Ge_{As}]/[Ge_{Ga}]$ , where  $[Ge_{As}]$  is the concentration of Ge acceptors on As sites and  $[Ge_{Ga}]$  the concentration of Ge donors on Ga sites, should be a sensitive diagnostic tool to study the steady-state arsenic surface population as a function of impinging dimeric and tetrameric arsenic species.

For a first qualitative estimation of this effect, Fig. 6 displays two shallow

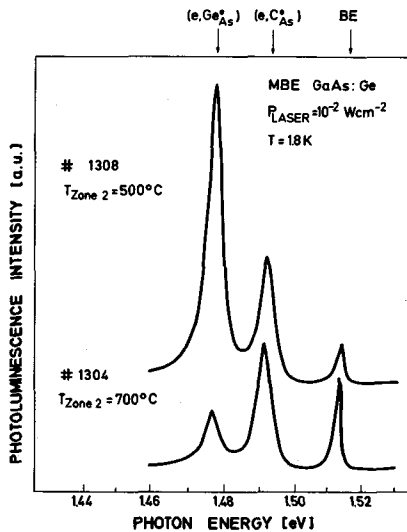


Fig. 6: Shallow acceptor 1.6 K PL spectra of MBE n-GaAs:Ge layers grown with different  $As_2/As_4$  flux ratios. The spectra are normalized in intensity to the peak height of the  $(e, A^0)$  transition related to  $C_{As}$ .

acceptor PL spectra of intentionally Ge-doped n-type GaAs films grown with different temperatures of the  $As_4$  cracking zone. In both spectra the two acceptors  $Ge_{As}$  and  $C_{As}$  can be clearly detected by their recombination radiation  $(e, A^0)$  of free electrons  $e$  captured at the corresponding neutral acceptors  $A^0$ . An increase of the amount of  $As_2$  relative to  $As_4$  species emerging from the arsenic source results in a marked reduction of the  $(e, A^0)$  luminescence transition related to Ge on As sites at 1.479 eV. The considerable decrease of the  $(e, A^0)$  intensity occurs at a cracker temperature of

700 °C. This is in good agreement with the behaviour of the defect induced bound exciton lines described in Sec. 3.1. The dimeric arsenic species replacing the tetrameric ones in the reaction provide a considerable higher arsenic surface population at the same arsenic-to-gallium flux ratio and substrate temperature. This drastically reduces the amount of As sites available for Ge incorporation on acceptor sites.

Based on a model including both C and Ge acceptors as well as Ge donors we could recently show [17] that the ratio of Ge autocompensation decreases exponentially with inverse substrate temperature, as depicted by the upper curve of Fig. 7, when using Ga and  $As_4$  molecular beams. The data of the temperature dependence of the Hall effect yielded the overall compensation ratio,  $N_A/N_D$ , and the data from detailed PL measurements were used to estimate the ratio of C and Ge acceptors incorporated on As sites. From that analysis we were thus able to determine the concentration of the three dominant impurities  $[Ge_{Ga}]$ ,  $[Ge_{As}]$ , and  $[C_{As}]$  separately.

When we applied the same evaluation procedure to GaAs:Ge samples grown from dimeric arsenic species only (generated by incongruent evaporation of GaAs), we obtained the concentrations summarized in Table 2. We also observed an exponential decrease of the Ge autocompensation ratio with inverse substrate temperature. Inspection of Fig. 7 reveals, however, that a much lower and therefore more favourable compensation ratio in n-GaAs:Ge can be achieved at a given substrate temperature with the use of  $As_2$  instead of  $As_4$  species. Autocompensation ratios as low as  $2 \times 10^{-2}$  have been obtained at a substrate temperature of 530 °C (of course this value does not include the additional compensating C acceptors). The observed behaviour of autocompensation of amphoteric dopants in MBE GaAs is thus directly correlated with the surface population of available free As sites for acceptor incorporation which can be more drastically reduced by an external flux of dimeric than tetrameric

arsenic species.

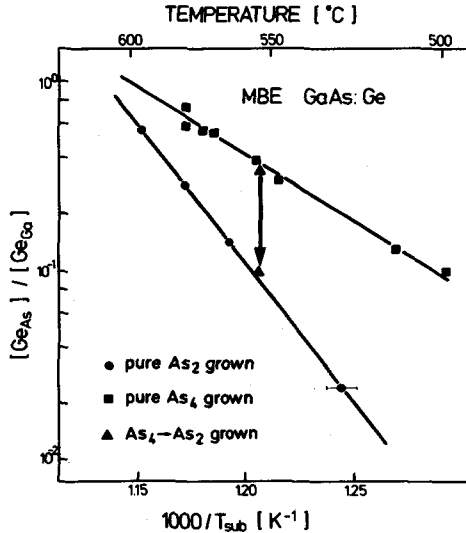


Fig. 7 : Substrate temperature dependence of Ge autocompensation ratio in MBE n-GaAs:Ge layers;

- samples grown from pure As<sub>4</sub> molecular beam species by evaporation of elemental arsenic.
- samples grown from pure As<sub>2</sub> molecular beam species by incongruent evaporation of GaAs.
- ▲ samples grown from an adjustable As<sub>2</sub>/As<sub>4</sub> ratio in the molecular beam by operating the two-zone effusion cell. The arrow indicates the reduction of autocompensation by increasing the As<sub>2</sub>/As<sub>4</sub> flux ratio.

Table 2. Concentration of C and Ge impurities on either Ga or As sites in MBE GaAs:Ge layers grown from pure As<sub>2</sub> molecular beam species at different substrate temperatures. Growth at 610 °C produces p-type material where the analysis of Hall data is not valid

GaAs:Ge	T <sub>Sub</sub> [°C]	[Ge <sub>Ga</sub> ] [cm <sup>-3</sup> ]	[Ge <sub>As</sub> ] [cm <sup>-3</sup> ]	[C <sub>As</sub> ] [cm <sup>-3</sup> ]	N <sub>A</sub> /N <sub>D</sub>	[Ge <sub>As</sub> ]/[Ge <sub>Ga</sub> ]
# 1222	530	5.2x10 <sup>16</sup>	1.2x10 <sup>15</sup>	2.9x10 <sup>16</sup>	0.59	0.024
# 1224	565	4.5x10 <sup>16</sup>	6.4x10 <sup>15</sup>	8.3x10 <sup>15</sup>	0.33	0.14
# 1225	580	8.6x10 <sup>16</sup>	2.4x10 <sup>15</sup>	3.3x10 <sup>15</sup>	0.66	0.28
# 1226	595	1.0x10 <sup>16</sup>	5.6x10 <sup>15</sup>	3.7x10 <sup>15</sup>	0.92	0.55
# 1228	610	-	-	-	>1	-

The other striking result indicated in Fig. 7 is that, nevertheless, with both arsenic species the transition of MBE GaAs:Ge layers, grown at a constant arsenic-to-gallium flux ratio of two, from n-type to p-type material occurs in the same substrate temperature range of 600 - 610 °C. The observed behaviour agrees well with earlier results of Neave and Joyce [18] in that the surface population of vacancies for Ge incorporation does not only relate to the external fluxes but is also influenced by the internal sources of both Ga and As. This reevaporation of the constituent elements from the growing surface depends strongly on the growth temperature. An increase of the substrate temperature at constant incident fluxes lowers the ratio of arsenic-to-gallium steady state adatom population, until at T<sub>Sub</sub> > 600 °C a change of the RHEED pattern from As-stable (2x4) via (1x1) to Ga-stable (4x2) is observed.

Finally, we demonstrate that the observed difference of Ge autocompensation is not caused by any additional impurities from the separate As<sub>2</sub> and As<sub>4</sub> sources. The black triangles in Fig. 7 indicate the results of two representative samples (# 1304 and # 1308) which were grown with different As<sub>4</sub>/As<sub>2</sub> ratios generated from

the two-zone effusion cell. A reduction of the Ge autocompensation ratio from 0.34 (# 1304) to 0.10 (# 1308), indicated by the arrow in Fig. 7, has been achieved simply by increasing the temperature of the  $\text{As}_4$  cracking zone to  $700^\circ\text{C}$ , where dimeric arsenic beam species dominate. This behaviour is consistent with the results of our PL measurements described earlier in the text.

**4. Conclusion.** - The optical and electrical properties of undoped and of Ge-doped MBE GaAs layers were studied as a function of the impinging arsenic molecular beam species. Tetrameric molecules ( $\text{As}_4$ ) were obtained by standard evaporation of elemental arsenic, whereas dimeric molecules ( $\text{As}_2$ ) were generated either by incongruent evaporation of GaAs in a separate source or by cracking of  $\text{As}_4$  in a single two-zone effusion cell. The results of combined Hall effect, low-temperature PL and DLTS measurements demonstrate that a direct correlation exists between the arsenic species used and the incorporation of point defects as well as of amphoteric dopants.

The low-temperature PL measurements confirm that our previous observation of defect induced bound exciton lines is indeed caused by the interaction of tetrameric arsenic species and not by any external impurity from separate source materials needed for  $\text{As}_2$  and  $\text{As}_4$ . The intensity of those extra emission lines between 1.504 and 1.511 eV can be reduced to below the detection limit by cracking  $\text{As}_4$  into  $\text{As}_2$  species in a single two-zone effusion cell arrangement.

The behaviour of the intensity of the defect related PL emission lines was found to be directly correlated with the concentration of three deep states (M1, M3, M4) which are characteristic of MBE GaAs films grown under As-stabilized (2x4) surface reconstruction. The concentration of the electron traps due to defect related deep centers may be easily modified by changing the impinging  $\text{As}_4/\text{As}_2$  flux ratio via the cracker temperature. Thus, a substantial reduction by a factor of five has been achieved, when a pure dimeric arsenic source is used.

Furthermore, we point out that the incorporation of point defect related centers as well as of amphoteric doping impurities is particularly sensitive to the surface chemistry involved. While  $\text{As}_2$  species impinging on the growing (100) GaAs surface undergo a rather elementary process of dissociative chemisorption (first-order process) involving a single Ga surface atom [2], the  $\text{As}_4$  species must encounter a pairwise interaction of relatively bulky units adsorbed on adjacent pairs of Ga surface atoms [1]. As a consequence, the steady-state arsenic surface concentration is much higher with impinging  $\text{As}_2$  than with  $\text{As}_4$ , all other growth conditions including the observed surface reconstruction being constant. This reduces considerably the amount of vacancies responsible for native defect formation as well as free As sites available for Ge incorporation as acceptors. In good accordance with our results on the intensity of the extra PL lines and on the concentration of deep traps we obtained substantially lower autocompensation ratios in Ge-doped n-GaAs samples using  $\text{As}_2$  instead of  $\text{As}_4$  as a source of arsenic.

For amphoteric dopant incorporation in MBE GaAs it is finally important to notice that the surface population of vacancies available for site occupation during growth does not only depend on the external fluxes but also on the internal sources of re-evaporating gallium and arsenic. While in agreement with Teramoto's theory [19] an external flux of  $\text{As}_4$  has only a minor influence on the slope of the autocompensation ratio  $[\text{Ge}_{\text{As}}]/[\text{Ge}_{\text{Ga}}]$  versus  $1/T$  plot, the external flux of  $\text{As}_2$  yields a much steeper slope of that relation indicating its strong influence on the steady-state surface population of free As sites available for Ge acceptor incorporation. This is a direct consequence of the increased growth surface coverage with arsenic arising from the rather elementary surface chemistry involved.

**Acknowledgement.** - This work was sponsored by the Bundesministerium für Forschung und Technologie of the Federal Republic of Germany.

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