On the formation of the Sb_{Ga} heteroantisite in metalorganic vapor-phase epitaxial GaAs:Sb

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Metalorganic vapor-phase epitaxial growth of GaAs doped with isovalent Sb is reported. By increasing the trimethylantimony concentration during growth the total Sb concentration was varied between 1×10^{17}–1×10^{19} cm^{-3}. A new deep level defect with an activation energy of the thermal emission rates of $E_c - 0.54$ eV is observed. The defect concentration increases with increasing As partial pressure and with increasing Sb doping. It is also found that the EL2 concentration decreases with increasing Sb doping. The new energy level is suggested to be the $0/+$ transition of the Sb_{Ga} heteroantisite defect. No photocapacitance quenching effect, reflecting a metastable state as seen for $EL2(As_{Ga})$, is observed for Sb_{Ga}.

GaAs lightly alloyed with Sb is an interesting material from the viewpoint of isoelectronic doping, which is known to affect the solid stoichiometry and thereby the concentration of native defects. Rytova, Soloveva, and Milvidski have reported that the presence of an isovalent impurity in a concentration of 1×10^{19}–1×10^{20} cm^{-3} leads to a considerable alteration in the concentration of point defects in the liquid-phase-epitaxy (LPE) grown GaAs.[1] Based on the results of their thermodynamic calculations Bloom and Woodall have predicted that antisites are the predominant defects in isoelectronically doped GaAs.[2] It has been suggested in several papers dealing with bulk- and LPE-grown GaAs that the role of antimony and indium is unique among isoelectronic dopants because they have larger atomic radii than gallium and arsenic, respectively, and thus they are effective in reducing the dislocation density.[2–5] Beneking and co-workers have shown that addition of In to a level of a few atomic percent during the GaAs LPE growth greatly reduces the dislocation density and the deep trap concentration in epitaxial layers.[4] However, experimental data concerning the effect of Sb doping on the deep levels in metalorganic vapor-phase-epitaxy (MOVPE) grown GaAs have not yet been available.

We have, therefore, studied GaAs doped with Sb where the epitaxial layers are grown using a horizontal MOVPE reactor (Epiquip VP502-RP). The epitaxial growth took place at atmospheric pressure and at a growth temperature of $T = 680$ °C as measured by a pyrometer. The total flow rate of Pd-diffused H_2 was held constant at 5 sl/min (sl = standard liters). The reactants were electronic-grade arsine (AsH_3, 10% diluted in H_2, Phoenix), trimethylgallium (TMGa, Epichem), and trimethylantimony (TMSb, Guangming Research Institute of Chemical Industry, China). The metalorganic bubblers were kept in temperature-controlled baths at -5.7 °C. The TMGa mole fraction, which is known to determine the growth rate of GaAs,[6] was 1.55×10^{-4}, resulting in a growth rate of 4 μm/h. The V/III ratio was 50, also in the undoped GaAs reference sample. The flow through the TMGa bubbler was 13.9 sml/min (sml = standard milliliters), the AsH_3 flow rate was 400 sml/min, and the flow through the TMSb bubbler was varied from 4 to 20 sml/min, which after different levels of dilution corresponds to 0.1–13.4 sml/min. The average thickness of the layers grown was about 4 μm.

Since no data on the Sb distribution coefficient in the case of MOVPE growth of Sb-doped GaAs were available, we used the value $k_{Sb} = 0.25$, evaluated from the curve given by Stringfellow for the $GaAs_{1-x}Sb_x$ alloy system.[6] Generally $k_{Sb} = x^s_{Sb}/x^v_{Sb}$, where indexes s and v indicate solid and vapor phases, respectively. For the MOVPE process, in the case of mixing on anion sublattice,

$$x^v_{Sb} = p^0_{TMSb}/(p^0_{TMSb} + p^0_{AsH3}),$$

where p^0 is the input partial pressure of the vapor components. Quantitative analyses of the grown samples using the secondary-ion mass spectroscopy (SIMS) technique, proton-induced x-ray analysis, and the x-ray double-rocking curve technique showed that the total concentration of Sb in the highest doped sample was $<5\times10^{19}$ cm^{-3}. Neglecting the pyrolysis efficiency of the source molecules, the value of k_{Sb} for the highest Sb doping level (20 sml/min flow rate) was thus determined to be ≈ 0.27. It was, however, found that the distribution coefficient depends on the Sb doping level. This will be further discussed in a coming publication.

Low-temperature (2 K) photoluminescence measurements on the Sb-doped samples showed the same principal emission bands as observed in the undoped samples, and in particular, no shift in the energy position of the band-edge luminescence was observed. This confirms that the Sb content in the epitaxial layers is less than 1%.

All epitaxial layers exhibited mirrorlike surfaces, but with increasing Sb mole fraction in the vapor phase specific features on the surface layer appeared. Similar behavior

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TABLE I. Growth and electrical parameters of Sb-doped GaAs.

Sample no.	TMSb flow[a] (sml/min)	TMSb MF[b] (10^{-6})	Carrier concentration (10^{14} cm^{-3})	N_T (Sb)[c] (10^{12} cm^{-3})	N_T (EL2)[c] (10^{12} cm^{-3})
166	0	0	0.79	0	12
170	0.10	0.47	3.5	0.20	13
169	0.21	1.1	1.0	0.28	4.6
167	3.43	17	3.84	1.7	3.6
168	13.33	64	1.4	2.8	3.3

[a]Flow through the TMSb bubbler. In order to obtain small TMSb flows a dilution method was used.
[b]MF is the mole fraction.
[c]The concentration values have not been corrected for the edge-region effects.

was observed by Chen and Wie in LPE-grown Sb-doped GaAs.[5] They reported an optimal Sb concentration of $2–3\times10^{19}$ cm^{-3}. Above this range dislocations and other extended defects generated a cross-hatched pattern on the surface. Since our maximum Sb doping was $<5\times10^{19}$ cm^{-3} we did not observe such an effect.

The free-carrier concentrations were measured by anodic dissolution and *in situ* capacitance-voltage (*C-V*) measurements on an electrolytic Schottky barrier using a Polaron semiconductor profile plotter, and by conventional *C-V* measurements on Schottky diodes. The Schottky diodes were prepared by evaporating an ohmic contact of Sn-Au-Cr on the *n* substrates followed by an alloying procedure at 450 °C (for 30 s) in a nitrogen atmosphere. A Schottky barrier of Au was then evaporated on the MOVPE layer. All layers, including the undoped reference sample, showed *n*-type conductivity and free-electron concentrations as described in Table I.

The layers were characterized by deep level transient spectroscopy (DLTS).[7] In order to avoid complete depletion of the epitaxial layer a low reverse bias of 0.8 V was used. The detection limit of the equipment was approximately $N_T/N_d=10^{-5}$, where N_T is the concentration of the deep level defect and N_d that of the shallow level dopant. Figure 1 shows a typical DLTS spectrum for one of the Sb-doped layers. It shows two different electron traps, each with a concentration that depends on the Sb doping and the stoichiometry (Table I). In the reference samples only the high-temperature peak was present. The temperature dependence of the thermal emission rates was measured for the two peaks. It was immediately recognized that the high-temperature peak is caused by the EL2 level,[8] while the low-temperature DLTS peak is, to the best of our knowledge, here reported for the first time.

In Fig. 2 the T^2-corrected thermal emission rates (e_n^t/T^2) of this new energy level are plotted as a function of the inverse temperature. The thermal emission rate for an electron trap is given by $e_n^t = \sigma_n v_{\rm th} N_c \exp(-\Delta G/kT)$, where σ_n is the electron capture cross section, $v_{\rm th}$ the thermal velocity of electrons in the conduction band, N_c the effective density of states in the conduction band, and ΔG ($=\Delta H - T\Delta S$, where ΔH is the enthalpy and ΔS the entropy) is the change in the Gibbs free energy.[9] The activation energy ΔE_a obtained from the Arrhenius plot in Fig. 2 is 0.54 eV. Here $\Delta E_a=\Delta H+\Delta E_c$ if the capture is thermally activated with an energy ΔE_c [i.e., $\sigma_n=\sigma_\infty \times\exp(\Delta E_c/kT)$]. This activation energy value does, therefore, not necessarily give the energy position in the band gap since the capture cross section of the deep level might be temperature dependent. An attempt to measure the capture cross section failed due to a strong nonexponential behavior of the capacitance signal as a function of different capture pulse widths.

With increased Sb doping the concentration of the new deep level defect increased, while at the same time the EL2 concentration decreased (see Table I). The EL2 level concentration fell from 1×10^{13} cm^{-3} in the undoped samples to 3×10^{12} cm^{-3} in the highest Sb-doped sample. The new deep level increased from low 10^{11} cm^{-3} in the lightest Sb-doped sample to 3×10^{12} cm^{-3} in the highest doped sample. This indicates that the two deep level defects compete for the same lattice site. In fact, the chosen V/III ratio (50) was the highest usable in practice, and was motivated by the increased concentration of the new defect. As a result also the EL2 level concentration was high, as ex-

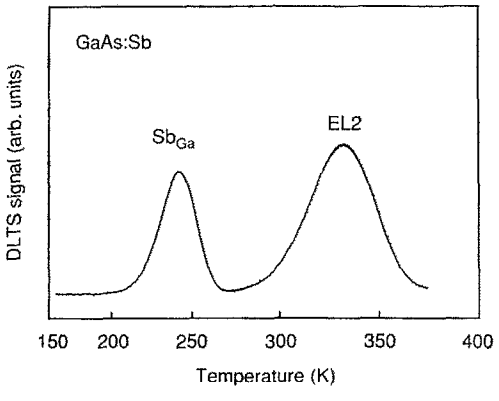

FIG. 1. A DLTS spectrum of an Sb-doped MOVPE-grown GaAs layer. The new, low-temperature peak is suggested to be identified as the Sb_{Ga}, and the high-temperature peak is the well-known EL2 level. The rate window is 2.4 s^{-1}.

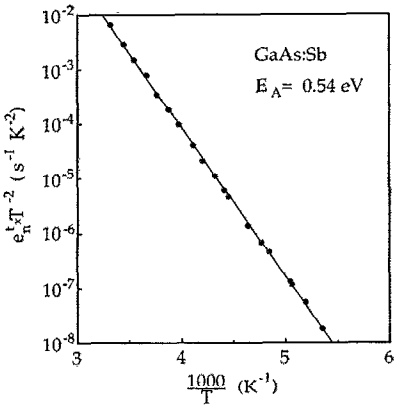

FIG. 2. The temperature dependence of the T^2-corrected thermal emission rates for the new energy level in GaAs. The data are obtained using both the DLTS and the single-shot dark capacitance techniques.

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pected for As-rich growth.[10]

The formation of the EL2 level appears to be governed by the number of available gallium vacancies at growth temperatures.[10] The available As atoms (As_i) recombine with the Ga vacancies and form the As_{Ga} antisite which is part (alone or in a complex) of the EL2 defect.[11–14] The decrease of the EL2 concentration when Sb doping is performed shows that the new defect probably is located on the Ga sublattice. The fact that the concentration of the new defect increases with increased Sb doping suggests that Sb is part of the defect. The simplest structure for the new defect is therefore Sb_{Ga}, even though Sb_{Ga}-containing complexes cannot be ruled out.

This identification of the energy level as being due to Sb_{Ga} is supported by previous findings in Sb-doped liquid-encapsulated Czochralski (LEC) GaAs material. Mitchel and Yu[15] reported on Hall measurements on a deep donor level at $E_c - 0.48$ eV which they suggested was the Sb_{Ga} heteroantisite, alone or in a complex. A more recent investigation of the same samples, using the electron paramagnetic resonance (EPR) and the photo-EPR techniques, by Baeumler *et al.*[16,17] convincingly identified the defect as being the isolated Sb_{Ga} heteroantisite and that the $0/+$ donor level of the defect is located at $\approx E_c - 0.5$ eV.

Furthermore, the growth of LEC GaAs is similar to the MOVPE growth from the stoichiometry point of view since both are As-rich growth methods. The Sb_{Ga} concentration in the above-mentioned LEC material was found to be in the same range as the EL2 concentration, and the generation efficiency of Sb on a Ga vacancy was about 1000 times that for As on a Ga vacancy. This is very similar to the present case of MOVPE growth, where the total concentration of Ga vacancies is less but where the ratio between the concentrations of EL2 (As_{Ga}) and Sb_{Ga} is the same as in the case of LEC growth. This indicates a similar generation efficiency in the LEC and MOVPE cases which further supports the identification.

It should be noted that the thermal emission rates and the activation energy of the new defect are very similar to the values reported for the EL3-level[18] and the O_{As} level[19] in GaAs. In fact, it was recently suggested that the EL3 defect is identical to the O_{As} defect.[20] There are, however, several arguments which make us suspect that the similar emission rates are only accidental. First, the concentration of the new defect increases with increasing the TMSb flow, while oxygen is unlikely to appear in the TMSb source because of its well-known reactivity with the metalorganic compounds. Second, the formation of O_{As} would be favored by a low V/III ratio (i.e., the opposite of what is observed). Third, measurements of the optical cross sections of the new defect[21] show that they coincide with those obtained by photo-EPR[17] on the $Sb_{Ga}+$ defect. However, this identification should be further investigated in the future.

In order to shed further light on the similarities and differences between the EL2(As_{Ga}) homoantisite and the Sb_{Ga} heteroantisite we have investigated the existence of a metastable state of Sb_{Ga} and a related photoquenching effect.[22] We conclude from our studies that no photoquenching effect, as reported for EL2, is observed for Sb_{Ga} in the photon range $0.5\ \text{eV} \leqslant h\nu \leqslant 1.5$ eV. This has been investigated at temperatures of 33 and 77 K, at which temperatures EL2(As_{Ga}) shows photoquenching.[22,23] This finding can be used as a test of models on antisite defects in GaAs.

To summarize, we have reported on successful MOVPE growth of GaAs doped with Sb in concentrations $< 5 \times 10^{19}\ \text{cm}^{-3}$. A new electron trap is detected by DLTS. Using space-charge techniques the thermal emission rates are measured as a function of temperature and an activation energy of 0.54 eV is determined. Based on the increased concentration of the defect with Sb doping, the stoichiometry conditions during growth, the anticorrelation with the EL2 level, the energy-level position of about $E_c - 0.5$ eV, and the similarities with the physical behavior of the Sb_{Ga} defect observed in LEC GaAs by Hall-effect, EPR and photo-EPR measurements, it is suggested that the new DLTS peak is caused by the $0/+$ transition of the Sb_{Ga} heteroantisite donor defect. No photocapacitance quenching effect, reflecting a metastable state as seen for EL2(As_{Ga}), is observed for Sb_{Ga}.

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[1] N. S. Rytova, E. V. Soloveva, and M. G. Milvidski, Sov. Phys. Semicond. **16**, 951 (1982).
[2] G. M. Bloom and J. M. Woodall, J. Electron. Mater. **17**, 391 (1988).
[3] G. Jacob, M. Duseaus, J. P. Farges, M. M. B. Ban Den Boom, and P. J. Poksnoer, J. Cryst. Growth **61**, 417 (1983).
[4] H. Beneking, P. Narozny, and N. Emeis, Appl. Phys. Lett. **47**, 828 (1985).
[5] J. E. Chen and C. R. Wie, J. Electron. Mater. **18**, 399 (1989).
[6] G. B. Stringfellow, *Organometalic Vapor Phase Epitaxy: Theory and Practice* (Academic, Boston, 1989).
[7] D. V. Lang, J. Appl. Phys. **45**, 3014 (1974); **4**, 3083 (1974).
[8] J. Lagowski, D. G. Lin, T. Aoyama, and H. C. Gatos, *Semi-insulating III-V Materials* (Shiva, Nantwich, 1984), p. 222.
[9] H. G. Grimmeiss and C. Ovrén, J. Phys. E **14**, 1032 (1982).
[10] L. Samuelson, P. Omling, H. Titze, and H. G. Grimmeiss, J. Cryst. Growth **55**, 164 (1981).
[11] D. T. J. Hurle, J. Phys. Chem. Solids **40**, 613 (1979).
[12] M. Kaminska, M. Skowronski, and W. Kuszko, Phys. Rev. Lett. **55**, 204 (1985).
[13] H. J. von Bardeleben, D. Stiévenard, D. Deresmes, A. Hubert, and J. C. Bourgoin, Phys. Rev. B **34**, 7192 (1986).
[14] B. K. Meyer, D. M. Hofmann, J. R. Niklas, and J. M. Spaeth, Phys. Rev. B **36**, 1332 (1987).
[15] W. C. Mitchel and P. W. Yu, J. Appl. Phys. **62**, 4781 (1987).
[16] M. Baeumler, J. Schneider, U. Kaufmann, W. C. Mitchel, and P. W. Yu, Phys. Rev. B **39**, 6253 (1989).
[17] M. Baeumler, F. Fuchs, and U. Kaufmann, Phys. Rev. B **40**, 8072 (1989).
[18] G. M. Martin, A. Mitonneau, and A. Mircea, Electron. Lett. **13**, 191 (1977).
[19] S. T. Neild, M. Skowronski, and J. Lagowski, Appl. Phys. Lett. **58**, 859 (1991).
[20] U. Kaufmann, E. Klausmann, and J. Schneider (unpublished).
[21] P. Omling, B. H. Yang, and L. Samuelson (unpublished).
[22] G. Vincent and D. Bois, Solid State Commun. **27**, 431 (1978).
[23] P. Omling, L. Samuelson, and H. G. Grimmeiss, Phys. Rev. B **29**, 4534 (1984).

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