Electronic properties of the Sb_{Ga} heteroantisite defect in GaAs:Sb

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The electronic properties of the Sb_{Ga} heteroantisite defect in epitaxial GaAs have been investigated using space-charge techniques. The energy-level structure of the defect is found to be consistent with that of a double donor with the $(0/+)$ energy level located at $E_c-0.5$ eV and the $(+/2+)$ energy level located at $E_c-0.7$ eV. The spectral distributions of the optical cross sections for three of the transitions have been measured in absolute numbers. A comparison with previously measured photo-EPR data on the Sb_{Ga}^{+} defect shows that the energy levels studied here originate in the Sb_{Ga} defect.

I. INTRODUCTION

Antisite defects in GaAs have been the subject of many theoretical and experimental investigations during recent years. Besides the fundamental interest in native defects, the attempts to identify the technologically important EL2 defect as the As_{Ga} antisite have motivated a substantial part of this research.[1] The question whether the EL2 defect is an isolated As_{Ga} or an antisite in a complex, and the well-known metastable properties of the EL2 defect, are still under investigation.

The As_{Ga} antisite defect is, however, not the only group-V antisite defect that has been observed in GaAs. Based on Hall-effect data on Sb-doped liquid-encapsulated Czochralski (LEC) GaAs an electron trap located at $E_c-0.48$ eV was suggested to be related to the Sb_{Ga} heteroantisite defect.[2] This has been confirmed by electron-paramagnetic resonance (EPR) investigations on the same material where the Sb_{Ga}^{+} heteroantisite defect was identified.[3,4] A photo-EPR investigation showed convincingly that the $0/+$ energy level of the Sb_{Ga} defect is located at about $E_c-0.48$ eV.[5] Recently, a deep-level transient spectrsocpy (DLTS) investigation of Sb-doped metal-organic vapor-phase epitaxy (MOVPE) grown GaAs showed a deep electron trap with a thermal activation energy of 0.54 eV.[6] This energy level was suggested to be the $0/+$ transition of the Sb_{Ga} heteroantisite defect.

A group-V atom on a group-III lattice site is expected to form a double donor. This has been observed with As_{Ga} in GaAs,[1] even though the exact atomistic nature of this defect is still debated. The experimental evidence of the double-donor nature of the As_{Ga} defect comes from spin resonant data,[7,8] magnetic circular dichroism data,[9] and, maybe most convincingly, from measurements of the electronic properties using space-charge techniques.[10] In the case of the Sb_{Ga} defect no detailed investigation of the electronic properties has been performed so far, and the double-donor nature of the defect, for instance, has still to be confirmed.

The purpose of this paper is, therefore, to report on electronic data obtained on the Sb_{Ga} defect in epitaxially grown GaAs:Sb samples using space-charge techniques. It will be argued that the defect, the concentration of which can be controlled by gas phase doping level and stoichiometric conditions, has two energy levels as expected when a group-V atom substitutes a group-III atom. The measured optical cross sections for three of the electronic transitions will be presented, and a comparison with the previously published photo-EPR data[5] on the $0/+$ transition of the Sb_{Ga} defect will be made. The data obtained on the Sb_{Ga} defect will, finally, be compared with what is known of the EL2 (As_{Ga} or As_{Ga}-complex) defect.

It should be noted that the identification of the EL2 level as the isolated As_{Ga} is debated. Several As_{Ga} containing defects have been observed.[11] It seems, however, that the electronic structure of the EL2 level is mainly determined by the As_{Ga} antisite defect. In order to simplify the presentation, we shall in this paper use the notation EL2 and As_{Ga} synonymously.

II. EXPERIMENTAL DETAILS

It is well known that the formation of As_{Ga} antisite defects is governed by the stoichiometric conditions during growth. As-rich growth conditions favor the formation of Ga vacancies and interstitial As. From those the As_{Ga} antisite defects are formed, with the concentration of available V_{Ga} as the limiting factor.[12] If Sb atoms are added to the crystal it has been observed that the probability that an Sb atom occupies the Ga vacancy is about 1000 times that of an As atom occupying the V_{Ga}.[3] This was concluded from the similar concentrations of As_{Ga} and Sb_{Ga} defects when the GaAs crystal was doped with Sb in the 10^{19}-cm^{-3} range. During LEC-growth of GaAs the concentration of V_{Ga} seems to be around 5×10^{16} cm^{-3}, while in vapor-phase epitaxy (VPE) growth the value is around $10^{13}-10^{14}$ cm^{-3}. Consequently, by doping VPE GaAs with 10^{19} cm^{-3} Sb, it should be possible to observe both the EL2- and the Sb-energy levels in the $10^{13}-10^{14}$-cm^{-3} range.

We have, therefore, studied GaAs doped with Sb where the epitaxial layers are grown using a horizontal MOVPE reactor (Epiquip).[6] The epitaxial growth took place at atmospheric pressure and at a growth temperature of $T=680\,^{\circ}C$. The total flow rate of Pd-diffused H_2 was held constant at 5 l/min. The reactants were electronic grade arsine (AsH_3, 10% diluted in H_2, Alfa), trimethylgallium (TMGa, Alfa) and trimethylantimony (TMSb, Guangming Research Institute of Chemical Industry in China). The metalorganic bubblers were kept in temperature-controlled baths at $-5.7\,^{\circ}C$. The TMGa mole fraction, which is known to determine the growth rate of Sb containing GaAs, was 1.55×10^{-4}, resulting in a growth rate of 4 μm/h. The AsH_3/TMGa partial-pressure ratio was 50, also in the undoped GaAs reference sample. The TMGa flow rate was 13.9 ml/min, the AsH_3 flow rate was 400 ml/min, and the TMSb flow rate was varied from 4 to 20 ml/min. The average thickness of the grown layers was about 4 μm.

Quantitative analyses of the grown samples using the secondary-ion-mass spectroscopy 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 $\approx5\times10^{19}$ cm^{-3}. Low-temperature (2 K) photoluminescence measurements on the Sb-doped samples showed the same principle 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 much less than 1%.

The free carrier concentrations were determined by C-V measurements on Schottky diodes. The Schottky diodes were prepared by evaporating an Ohmic contact of Sn-Au-Cr on the n-type substrates followed by an alloying procedure at 450 °C (for 30 sec) in a nitrogen atmosphere. A Schottky barrier of Au was then evaporated on the MOVPE layer. The samples showed n-type conductivity and free electron concentrations around 1×10^{15} cm^{-3}.

For the study of thermal emission rates of electrons, both DLTS (Ref. 13) and dark-capacitance single transient techniques were used.[14] The optical emission rates were determined by photocapacitance transient spectroscopy.[14] The cross sections were evaluated using the time constants for the full transients, or by using the initial slope of the transients.

III. EXPERIMENTAL RESULTS

A DLTS spectrum obtained on one of the Sb-doped samples is shown in Fig. 1. It shows two different electron traps, each with a concentration which depends on the Sb doping and the stoichiometry conditions during growth. In the reference samples only the high-temperature peak was present. The high-temperature peak has been identified as the EL2 level, while the low-temperature DLTS peak has been suggested to be the Sb_{Ga} defect.[6]

In Fig. 2 the T^2-corrected thermal emission rates (e_n^t/T^2) of the Sb_{Ga} energy level are plotted as a function of the inverse temperature. The thermal emission

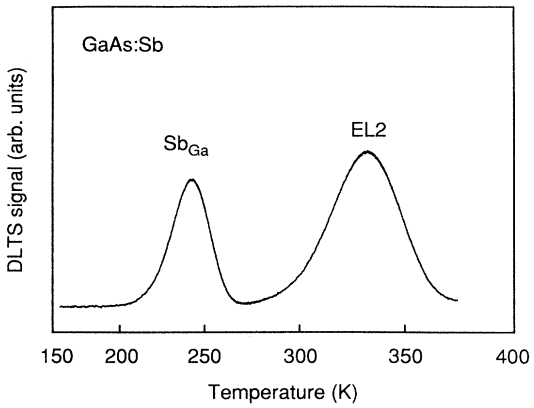

FIG. 1. DLTS spectrum of an Sb-doped MOVPE-grown GaAs layer. The rate window is 2.4 s^{-1} (from Ref. 6).

rate for an electron trap is given by $e_n^t=\sigma_n v_{th} N_c \exp(-\Delta G/kT)$, where σ_n is the electron capture cross section, v_{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.[14] 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., $\sigma_n=\sigma_\infty\exp(-\Delta E_c/kT)$]. An attempt to measure the capture cross section failed because of strong nonexponential behavior of the capacitance signal as a function of different capture pulse widths. The measured activation energy, therefore, does not necessarily give the energy position in the band gap.

As expected, the concentration of the Sb_{Ga} defect was determined by the doping and stoichiometry conditions

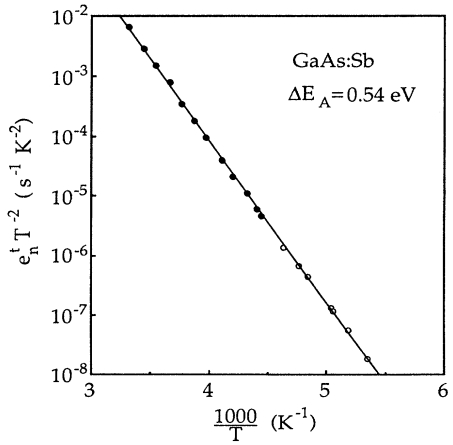

FIG. 2. Temperature dependence of the thermal emission rates for the Sb_{Ga} energy level in GaAs (T^2 corrected). The data are obtained using both the DLTS (solid circles) and the single shot dark capacitance (open circles) techniques.

during growth. With increased Sb doping the concentration of the Sb_{Ga} defect increased, while at the same time the EL2 concentration decreased. The EL2 level concentration fell from almost 10^{13} cm^{-3} in the undoped samples to 2×10^{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 2×10^{12} cm^{-3} in the highest-doped sample. The data confirm that the two antisite defects compete for the same lattice site, and the concentrations agree with those expected from the discussion above. In order to obtain as high an Sb_{Ga} concentration as possible, a high AsH_3/TMGa partial-pressure ratio was used during growth. As a result also the EL2 level concentration was high, as expected for As-rich growth.[12]

The estimated concentrations of the defects as determined from the photocapacitance signals at $T=77$ K agree, within experimental uncertainties, with those obtained from the DLTS measurements. The quenchable part [i.e., EL2 quenching using $h\nu=1.1$ eV (Ref. 1)] of the capacitance transients corresponds to the EL2 concentration, and the remaining part is consistent with the Sb_{Ga} concentration, as determined by DLTS. Here the values of the optical cross sections at $h\nu=1.1$ eV (determined below) have been taken into account.

Even though the samples are virtually free from disturbing deep-level defects, the unavoidable high EL2 concentration, discussed above, causes considerable complications in the analyses of the photocapacitance transients of the Sb_{Ga} defect. Besides the charge-transfer processes related to EL2 (of similar magnitudes to those of the Sb_{Ga} level), measurements at $T\leq100$ K are further disturbed by the optically induced transfer of the EL2 defect to its metastable state.[1,15] In order to avoid those complications we have carefully chosen a measurement temperature of $T=33$ K. At this temperature the diode is still working properly, while it is possible to transfer the EL2 levels to the metastable state, and more important, to keep them there. This is a result of the temperature dependence of the electrical regeneration mechanisms of the EL2 defect which prevents the defect from interacting with free carriers at low temperatures.[15] The result is that once the EL2 defects are transferred to the optically nonactive metastable state they are (from an optical and charge-transfer point of view) not present in the sample. In such a way we have obtained a suitable sample in which the optical investigations on the Sb_{Ga} defect can be performed.

For measurements of the photocapacitance transients all deep Sb_{Ga} levels (concentration N) in the space-charge region of a diode are filled with electrons ($n_0=N$) by zero biasing the diode. Illuminating the reverse biased sample with monochromatic photons allows the observation of the change of the capacitance signal when the occupation of the deep levels changes. The rate equations for the Sb_{Ga} double-donor system (Fig. 3) at low temperatures are given by

$$dn_0/dt=(-\sigma^o_{n1}n_0+\sigma^o_{p1}n_+)\phi\ , \tag{1}$$

$$dn_+/dt=(\sigma^o_{n1}n_0-\sigma^o_{p1}n_+-\sigma^o_{n2}n_++\sigma^o_{p2}n_{2+})\phi\ , \tag{2}$$

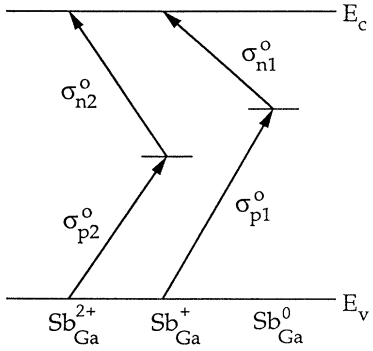

FIG. 3. Energy-level structure of the double-donor Sb_{Ga} defect. The charge states of the defect and the optical transitions are also shown.

$$dn_{2+}/dt=(-\sigma^o_{p2}n_{2+}+\sigma^o_{n2}n_+)\phi\ , \tag{3}$$

$$N=n_0+n_++n_{2+}\ , \tag{4}$$

where n_0 is the number of neutral defects, n_+ the number of singly ionized defects, n_{2+} the number of doubly ionized defects, and ϕ the photon flux. The other symbols are defined in Fig. 3. For $h\nu<0.7$ eV all cross sections except σ^o_{n1} are equal to zero, and a solution is given by $n_0(t)=N\exp(-\sigma^o_{n1}\phi t)$. The capacitance signal is proportional to the occupation, so the optical cross section can be determined in absolute numbers directly from the time constant of the capacitance signal if the photon flux is known. Another way to determine the optical cross section, also in the region where $h\nu>0.7$ eV, is to use the initial slope technique.[14] From Eqs. (1)–(4) it is easily seen that the initial slope of the capacitance transient is proportional to σ^o_{n1} when $n_0=N$.

Before these measurement techniques can be applied, the exponentiality of the capacitance transients has to be investigated. Figure 4(a) shows an example of the perfect single exponential transients obtained for $h\nu<0.7$ eV, indicating that the measurement is performed on only one energy level. However, for $0.7<h\nu<1.0$ eV the transients are double exponential showing the contribution from two energy levels [Fig. 4(b)]. For higher energies the transients are dominated by one transient but, again, are double exponential. In Fig. 5 the total capacitance change as a function of photon energy is plotted as open circles. Also shown is the magnitude of the first transient (dashed line). The capacitance changes for the two transients add up to the total value. The conclusions from these data are that (see Fig. 3) the σ^o_{n1} ionization from the neutral to singly ionized Sb_{Ga} defect (0/+) starts at $h\nu\approx0.5$ eV. At $h\nu\approx0.7$ eV the +/2+ ionization occurs (σ^o_{n2}). This increases the capacitance change by a factor of 2 (see Fig. 5). At $h\nu\approx0.75$ eV the capacitance change decreases, corresponding to the neutralization of the Sb_{Ga}^{2+} defect (σ^o_{p2}). At energies ≥1 eV all optical transitions are active simultaneously and the magnitude of the capacitance change varies according to the relative magnitudes of the optical cross sections. We conclude

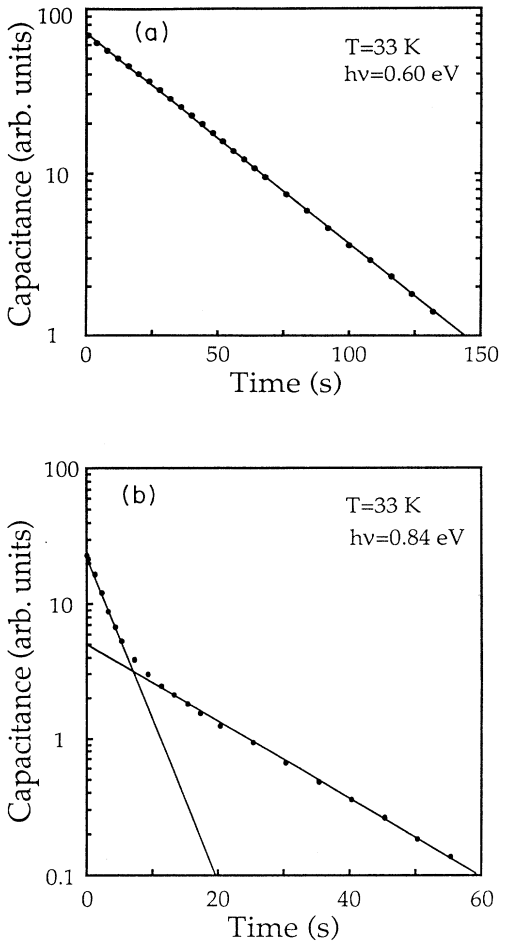

FIG. 4. Photocapacitance transients obtained at (a) $h\nu=0.60$ eV and (b) $h\nu=0.85$ eV.

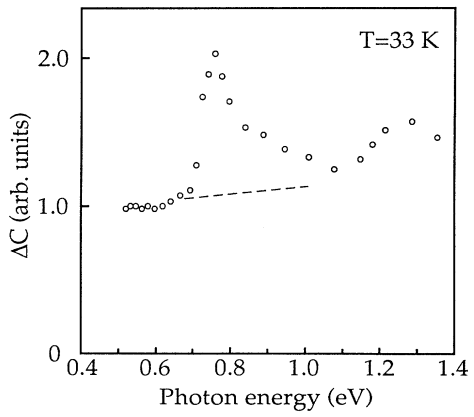

FIG. 5. Total capacitance change upon optical illumination as a function of photon energy. The dashed line indicates the magnitude measured on one of the transients in the bi-exponential region.

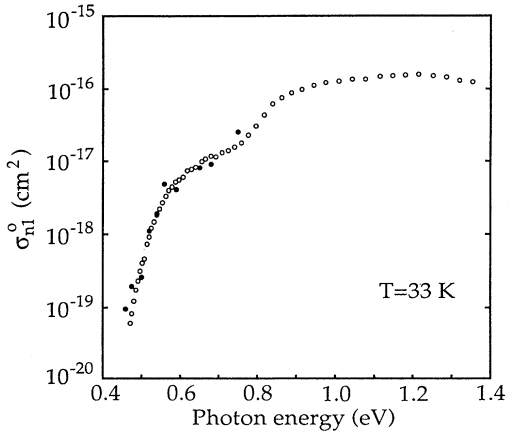

FIG. 6. Optical cross sections for the Sb_{Ga} 0/+ ionization transition σ^o_{n1} obtained by photocapacitance measurements (open circles, this work) and by photo-EPR measurements (solid circles, from Ref. 5).

that the experimental data are not in disagreement with the double-donor model.

Our next task is to measure the optical cross sections. The absolute values of the σ^o_{n1} cross sections as a function of photon energy are shown in Fig. 6. The cross sections are measured using both the full transients and the initial slope technique as described above. The spectrum consists of a threshold at about 0.5 eV and a marked increase at 0.8 eV, which, at first glance, may appear like the superposition of spectra obtained on two deep levels. However, the data are measured only on the first transient, which is single exponential (i.e., the single transient for $h\nu<0.7$ eV and, for higher energies, the capacitance signal indicated by a dashed line in Fig. 5). It can, therefore, be concluded that the complete spectrum in Fig. 6 originates only from the $Sb_{Ga}^{0/+}$ transition. The two steps, separated by ≈ 0.3 eV, might originate in the

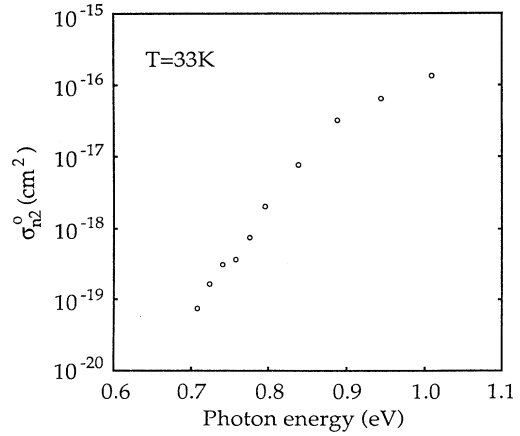

FIG. 7. Optical cross sections for the Sb_{Ga} +/2+ ionization transition (σ^o_{n2}).

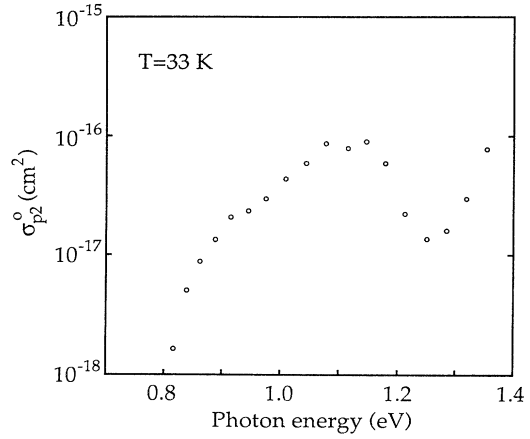

FIG. 8. Optical cross sections for the Sb_{Ga} 2+/+ neutralization transition (σ^o_{p2}).

different density of states in the Γ- and *L*-conduction bands.[1]

The measurements of the σ^o_{n2} cross sections were performed in the following way. The sample was illuminated with a strong pump light at $h\nu \approx 0.6$ eV, which transfers all defects to the positive charge state, i.e., $n_+ = N$ and $n_0 = n_{2+} = 0$. From Eqs. (1)–(4) it can be seen that with these initial conditions only σ^o_{n2} and σ^o_{p1} can be measured in an initial slope measurement. By keeping the strong pump light on, no defects are transferred to the neutral state. From a subsequent initial slope measurement of the capacitance change, the σ^o_{n2} cross section can be obtained. The results are shown in Fig. 7. It should be noted that the results are similar also if the strong pump light is not used during the initial slope measurements indicating that the σ^o_{p1} cross section is small.

At $h\nu = 0.78$ eV the capacitance change shows that the defect seems to be completely transferred to the doubly ionized state (see Fig. 5). Consequently, it is possible to use the initial slope technique to measure the σ^o_{p2} cross sections. The results are shown in Fig. 8.

We have also investigated the possible existence of a metastable state of Sb_{Ga}. From a comparison with EL2 (As_{Ga}) such a state might be expected. In the case of EL2 (As_{Ga}) the metastability is observed as a photocapacitance quenching effect.[1,15,16] We conclude from our studies on the two Sb_{Ga} energy levels that no sign of photoquenching is observed. This has been investigated from $0.5 < h\nu < 1.5$ eV at $T = 33$ and 77 K.

IV. DISCUSSION

It has been noted that the thermal emission rates for the Sb_{Ga} defect are very similar to those reported for the EL3 defect.[6] The EL3 defect has recently been argued to be identical to an oxygen atom occupying an As substitutional lattice site, O_{As} (slightly distorted).[17,18] An important question is therefore whether the defects labeled Sb_{Ga}, O_{As}, and EL3 are identical or if the similar emission rates are only accidental. Here we shall discuss the identification of the Sb_{Ga} defect and shall stress the differences with the O_{As} defect.

The identification of the defect discussed in this paper as Sb_{Ga} comes from the following arguments. First, the defect is introduced in our MOVPE GaAs by Sb doping. The Sb source is a metal-organic compound (TMSb) which is very reactive with oxygen, and oxygen contamination is therefore not likely. Second, the defect is formed in As-rich conditions, which is consistent with a defect formed on Ga vacancies, but contrary to what is expected for defects like O_{As}, located on the As lattice sites. Third, as mentioned above the "generation efficiency" of the Sb_{Ga} defect, compared with the As_{Ga} defect in MOVPE samples is the same as observed in the LEC material.[2] Fourth, the thermal energy position of the first ionization transition measured in the MOVPE samples agrees with the position measured in the LEC material. Fifth, the optical cross section for the first ionization cross section measured here agrees with the optical cross sections measured by photo-EPR (Ref. 5) on the chemically identified Sb_{Ga} defect (see Fig. 6). Sixth, the photocapacitance results are consistent with a model in which the defect is a double donor as expected for an Sb_{Ga} defect. A double donor character is less likely for the O_{As} defect.

Based on these arguments we feel confident that the defect under study is the Sb_{Ga} heteroantisite defect, and that it behaves as a double donor. Unfortunately, to the best of our knowledge, no photocapacitance investigation of the O_{As} (or the EL3) level has been performed. However, since the identification of the O_{As} level is based on apparently strong arguments, we suggest that the similar emission rates are only accidental.

The energy levels of the As_{Ga} antisite defect are at low temperatures located at $E_c - 0.74$ eV (0/+) and $E_v + 0.52$ eV (+/2+),[10] and for Sb_{Ga} at $E_c - 0.5$ eV (0/+) and at $E_c - 0.7$ eV (+/2+). It is interesting to note that the energy difference between the first and the second ionization levels is very similar for As_{Ga} and Sb_{Ga}, even though the ionization energies are smaller in the Sb_{Ga} case. This is, apparently, a further argument for the correct assignment of the energy-level structure of the Sb_{Ga} defect, and a motivation for the labeling of the defect as a heteroantisite in GaAs. However, the observed energy difference of 0.2 eV is often observed between different charge states of defects in III-V semiconductors.

The absence of a photocapacitance quenching effect for the Sb_{Ga} heteroantisite indicates that the defect has no metastable state or, alternatively, cannot be observed to transform to the metastable state. This is an important contrast to the EL2 (As_{Ga}) homoantisite. It is interesting to note that based on a calculation of total energies and electron structures of anion-antisite defects it was recently argued[19] that the optically inducible transformation to the metastable configuration is inefficient for Sb_{Ga} in GaAs.

V. CONCLUSIONS

From an investigation, by space-charge techniques, of MOVPE-grown GaAs doped with $\approx 10^{19}$-cm^{-3} Sb, the energy-level structure of the Sb_{Ga} defect has been deduced. The electronic structure of the defect is consistent with that of a double donor with the first ionization level $(0/+)$ at $E_c - 0.5$ eV and the second $(+/2+)$ at $E_c - 0.7$ eV. The thermal activation energy of the $0/+$ transition is 0.54 eV. Three of the optical cross sections (σ^o_{n1}, σ^o_{n2}, and σ^o_{p2}) have been measured in absolute numbers. The absence of photocapacitance quenching indicates that Sb_{Ga} has no metastable state or, alternatively, cannot reach the metastable state optically.

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