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Vacancy-associated Te sites in GaAs

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Defect structures, observed by ^{129}I Mössbauer spectroscopy in high-dose Te-doped GaAs, are identified by a reference study of the semiconducting compound Ga_2Te_3. The formation of Te_{As}-V_{Ga} complexes (tellurium atoms quasisubstitutional on an As site with a gallium vacancy in the first-neighbor shell) is proposed, in agreement with theoretical predictions. The relevance of this assignment in relation to the earlier proposed Te *DX* configuration is also discussed.

The lattice-site configuration of donor-related defects in GaAs has been extensively studied, mainly in connection with the saturation of the electrical activity observed for high dopant concentrations ($\geq 3\times10^{18}$ cm^{-3}), and with the phenomenon of persistent photoconductivity related to the formation of a deep metastable state, the so-called *DX* center.[1-9] The latter defect most commonly is found in $Al_xGa_{1-x}As$ for $x > 0.22$, but appears in GaAs at doping levels $\simeq 2.10^{19}$ cm^{-3}.[10] Various conflicting models have been proposed to explain the *DX* configuration.[10] Recently a consistent interpretation concerning the phenomenon of free-carrier saturation was developed based on the concept of amphoteric native defects.[11,12] Calculations showed that the total defect energy of group-III vacancies in GaAs decreases with increasing Fermi energy; hence, an abundance of the Ga vacancy (giving rise to three acceptor levels), was predicted in *n*-type substrates.[11] Based on these results, Walukiewicz explained the saturation of the free-carrier concentration, actually the cube-root dependence on the doped donor concentration, by the increased formation of (triply negatively ionized) Ga vacancies.[12] Pairing of the positively charged donor atoms with these acceptors, stabilized by the Coulomb interaction, is expected to occur.[13] Evidence in favor of this defect type was given by photoluminescence measurements,[1,8] slow positron beam annihilation experiments,[14] and by diffusion studies.[15] Results of local-vibrational-mode spectroscopy on Si-doped GaAs were interpreted as showing, in addition to the formation of Si_{Ga}-Si_{As} pairs, the presence of Si_{Ga}-V_{Ga} and Si_{As}-V_{Ga} complexes.[6]

Recently, ^{129}I Mössbauer spectroscopy (in the decay of ^{129m}Te) was applied to study the lattice-site configuration of the I probe atoms in high-dose Te-doped GaAs, doped by laser-assisted indiffusion,[16,17] and by implantation followed by a 900 °C annealing step.[5,18] Similar sets of hyperfine parameters were observed as a result of both types of processing. Part of the implantation data can be explained by the formation of *DX* centers, an interpretation which is strongly supported by the observation of persistent photoionization.[18] A Te site, characteristic for a highly disordered GaAs matrix was proposed to account for the observed correlation between the Mössbauer and *I-V* data obtained from the laser mixed Au/Te/Au/GaAs contacts.[16]

In this paper, an extensive reference study of Ga_2Te_3 by ^{129}I Mössbauer spectroscopy is presented. The results of this study allow one, due to the close similarity between the GaAs and Ga_2Te_3 (both covalent) lattice structures, to label the major part of the observed Te-GaAs defects as Te_{As}-V_{Ga} complexes (tellurium atoms quasisubstitutional on an arsenic site with a gallium vacancy in the first neighbor shell). This proposed Te defect configuration can also account for the observed anomalous electrical behavior of the laser mixed Au/Te/Au/GaAs contacts, the analysis of which is conducted in Ref. 17. The relevance of this interpretation for the earlier characterized Te *DX* configuration (Ref. 18) is also discussed.

The preparation procedure of ^{129m}Te labeled Ga_2Te_3 is described in Ref. 19, and experimental details about the Te-GaAs experiments are given in Refs. 5 and 16–18. ⟨100⟩ oriented GaAs wafers were used in all experiments. The Mössbauer data were recorded with the sources at 4.2 K, using a 10 mg/cm^2 CuI absorber, also at 4.2 K. In the interpretation of the Mössbauer data one has to take into account the fact that the actual Mössbauer transition occurs in the ^{129}I daughter nuclei of the implanted or indiffused ^{129m}Te probes. ^{129m}Te has a lifetime of 33.5 days and decays partly under β^- emission (recoil energy $\simeq 7$ eV) to the excited $\frac{5}{2}^+$ level in ^{129}I (lifetime 16.8 ns). The Mössbauer experiment uses the 27.8-keV $\frac{5}{2}^+ \rightarrow \frac{7}{2}^+$ transition in ^{129}I, therefore the probed electronic configuration reflects the I host (instead of the Te host) electronic bonds, whereas the investigated site occupation is determined by the parent Te atom.[20-22] In order to account for this dichotomy, the Te-related defect structures as probed by I are referred to as Te(I) centers when the lattice-site configuration is emphasized, and as I_{Te} defects in case the measured hyperfine fields (local electronic configurations) are discussed.

In the first part of this paper, the ^{129}I Mössbauer mea-

surements on Ga_2Te_3 are discussed. Ga_2Te_3 has, as a representative of the class of III_2-VI_3 semiconductors, like GaAs, the tetrahedral zinc-blende structure (with $d_{Ga_2Te_3}=5.899$ Å whereas $d_{GaAs}=5.653$ Å); it is, however, structurally defective in that one-third of the Ga sublattice positions remain vacant. Therefore, two-thirds of the Te atoms are surrounded by three-nearest-neighbor Ga atoms and one vacancy (Te:3Ga,1V), whereas the other third has two Ga atoms and two vacancies (Te:2Ga,2V) as nearest neighbors.[23] As can be seen in Fig. 1, a two-component fit (I_{Te}:3Ga,1V; I_{Te}:2Ga,2V) with a 2:1 intensity ratio, according to this micro-ordered structure[23] (the absence of a regular repetition of the Ga_2Te_3 unit cell was shown by x-ray diffraction[24]), yields a very reasonable fit quality ($\chi^2=1.44$). The corresponding fit values are given in Table I; the parameters quoted by Mo *et al.* are also listed [indicated by (MO 90)].[25] Thus, field gradients of this magnitude, namely, a quadrupole splitting $\Delta(eQV_{zz}/h)=+360(10)$ MHz, with an asymmetry parameter $\eta=0$, and $\Delta=+520(30$ MHz, $\eta\simeq 1$, are proposed to characterize the covalent bonded I_{Te}:3Ga,1V and I_{Te}:2Ga,2V sites in Ga_2Te_3. These site-field gradient associations are not only justified by the intensity ratio of the two components (in which no correction for a possible, though presumably small, difference in recoilless fraction between the two sites is made), but also by the very different η values, $\eta=0$ indicates a trigonal or higher symmetry, and hence is consistent with the I_{Te}:3Ga,1V site.

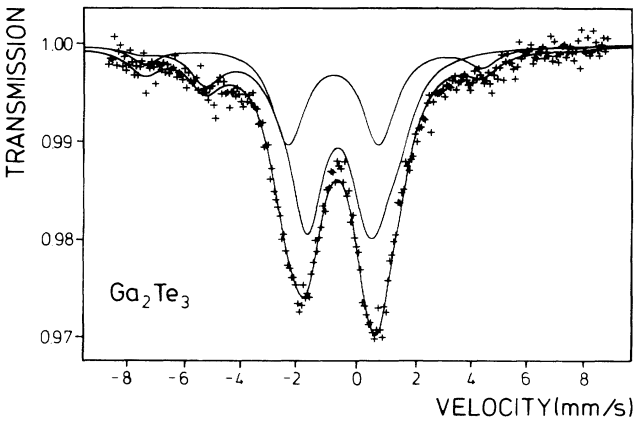

FIG. 1. ^{129}I Mössbauer spectrum of Ga_2Te_3, using a CuI absorber, fitted with two components (I_{Te},3Ga,1V; I_{Te},2Ga,2V).

Due to the close similarity between the GaAs and

TABLE I. ^{129}I Mössbauer parameters of two component fits to the spectrum of Ga_2Te_3 (I_{Te}:3Ga,1V; and I_{Te}:2Ga,2V), and to the spectra of pulsed laser mixed Au/(^{129}Te)Te/Au/GaAs structures and ^{129m}Te-implanted GaAs (singlet+multiplet). Reference Ga_2Te_3 fit—data reported by Mo *et al.* are also included (MO 90). The symbols δ, Δ, and η are defined in the text. Γ is the full linewidth at half maximum and was in our fit procedure kept equal for both components, F is the fractional resonance area. Isomer shifts are absorber isomer shifts given with respect to CuI.

	Spectral component	δ (mm/s)	Δ (MHz)	η	Γ (mm/s)	F (%)
			Ga_2Te_3			
This work	3Ga,1V	+0.82(5)	+369(10)	0	1.3(1)	67
	2Ga,2V	+0.94(5)	+550(10)	0.74(5)		33
(MO 90)	3Ga,1V	+0.82(5)	+349(10)	0	1.4(1)	67
	2Ga,2V	+0.77(5)	485(10)	1	1.2(1)	33
			Pulsed laser mixed Au/Te/Au/GaAs			
0.35 J/cm^2	singlet	+0.68(5)			1.4(1)	4
5 pulses	multiplet	+0.90(5)	+297(10)	0		96
0.55 J/cm^2	singlet	+0.63(5)			1.6(1)	42
5 pulses	multiplet	+0.88(5)	+325(10)	0		58
0.85 J/cm^2	singlet	+0.72(5)			1.4(1)	12
1 pulse	multiplet	+0.97(5)	+327(10)	0		88
0.85 J/cm^2						
5 pulses	multiplet	+0.92(5)	+339(10)	0	1.5(1)	≃100
2.5 J/cm^2						
1 pulse	multiplet	+0.91(5)	+343(10)	0	1.4(1)	100
			Te-implanted GaAs			
10^{13} atoms/cm^2	singlet	+0.70(5)			2.2(1)	100
5×10^{14}	singlet	+0.70(5)				10
atoms/cm^2	multiplet	+0.90(5)	+290(10)	0	2.0(1)	90
10^{16} atoms/cm^2	multiplet	+0.82(5)	+342(10)	0	1.7(1)	100

Ga_2Te_3 lattice structures, similar field gradients (within a deviation $\leq 10\%$, see below) are expected for identical I_{Te}-impurity first-neighbor defect configurations in GaAs. By the $1/r^3$ dependence of the quadrupole interaction strength, namely, a significant contribution to the electric-field gradient (EFG) at impurity nuclei is given only by the first- and second-nearest-neighbor shell (valence) charge distribution. This was shown explicitly by cluster calculations based on the self-consistent–charge-extended Hückel procedure applied for covalent lattices.[21,22] In these structures the field gradient due to the lattice point charges is (negligibly) small compared to the valence contribution, especially for iodine which has a very small ($R \simeq 0.03$) Sternheimer shielding factor.[21,22] A significant difference in the EFG values in GaAs and Ga_2Te_3 could arise from the difference in lattice parameter, as it was shown that shifts of the probe atoms in host matrices over $\simeq 0.1$ Å can change the EFG by as much as 30%.[21,22] However, in for instance the single vacancy Te-GaAs defect complex, a relaxation of the Te donor towards the vacancy, adjusting in this way the Ga-Te tetrahedral radii, is expected. This assumption is compatible with recently performed particle-induced x-ray emission spectroscopy channeling measurements on Te- and Sn-doped $Al_xGa_{1-x}As$.[9] Most definite evidence in favor of this is given by extended x-ray-absorption fine-structure measurements, which showed a contraction, and expansion, of the first-neighbor shell distances in S-GaAs (Ref. 3) and Te-GaAs (Ref. 4) systems, respectively; the values quoted closely follow the sum of covalent radii for both host-impurity combinations.[13] Hence, the major difference in electric-field gradients probed at the I_{TE} defective sites in both compounds will be due to the different hybridization of both semiconductors, being $(sp^3)^+_{1,2}$ and $(sp^3)^+$ for Ga_2Te_3 and GaAs, respectively.[13] As this difference only concerns the second sphere surrounding of the impurity atoms, the resulting influence on the observed field gradient will be a slightly larger (at most 10%) value for Ga_2Te_3 compared to GaAs. Thus, the I_{Te}:3Ga,1V defect complex (Te_{As}-V_{Ga} lattice-site configuration) in GaAs is expected to be characterized by a field gradient $\simeq +320$–360 MHz.

The results of ^{129}I Mössbauer measurements of Te-doped GaAs are summarized in Table I. The data of Te-implanted and postannealed (900 °C) GaAs were taken from Refs. 5 and 18, and those of the laser mixed structures from Refs. 16 and 17. The data of the laser-annealed as well as the Te-implanted samples were consistently fitted by a sum of two components (singlet plus multiplet), the intensities and parameters of which were left free in the subsequent iterations. Both processing methods clearly resulted in the formation of identical Te(I) sites (at least with regard to the first-neighbor shell configuration). One site, characterized by a single line component (isomer shift $\delta = 0.70$ mm/s), was shown to correspond to the $Te(I)_{As}$ substitutional site.[5] The second site, characterized by $\Delta = +290(10)$ MHz, $\eta = 0$, $\delta = 0.90(5)$ mm/s, was identified as the ^{129}I Mössbauer trace of the Te DX center configuration by the direct correlation of the intensity of this spectral component to the phenomenon of persistent photoconductivity.[18] Also, a field gradient of the same magnitude was observed in low dose (10^{13} atoms/cm^2) ^{129m}Te-implanted $Al_{0.6}Ga_{0.4}$-As samples [$\Delta = +305(10)$ MHz, $\eta = 0$].[18] Furthermore, the (DX) feature of a light-induced persistent electrical activity was confirmed for GaAs implanted under the same conditions with stable isotopes of tellurium and of iodine.[18] This DX identification, for the 10^{15} atoms/cm^2 GaAs-implant condition, however, accounted for only $\simeq 10\%$ of the intensity of the observed quadrupole multiplet.[18] Therefore, the presence of a third Te site characterized by a similar set of hyperfine parameters must be assumed. Hereto, we propose the $\Delta = +340(10)$ MHz, $\eta = 0$, $\delta = +0.90(5)$ mm/s multiplet, which is distinctly observed in the Mössbauer spectra obtained from the 10^{16} atoms/cm^2 implanted GaAs samples and from the 2.5 J/cm^2–1 pulse, and 0.85 J/cm^2–5 pulses laser-irradiated structures.

The possibility that the $\Delta = +340$ MHz multiplet would be a (deformed) trace of Ga_2Te_3 precipitates can be denied, although evidence for Ga_2Te_3 clustering was reported from earlier Mössbauer investigations of high-dose Te-doped GaAs.[26,27] X-ray diffraction and Raman measurements on our laser-irradiated samples did only show the presence of Ga_2Te_3 for the 0.35 J/cm^2 irradiation, but not for the 0.55, 0.85, and 2.5 J/cm^2 conditions,[28] which is consistent with our earlier Mössbauer results.[16] Raman measurements of the high-dose implanted GaAs samples excluded the possibility of a Ga_2Te_3 clustering as a result of this processing method as well.[28]

As the observed field gradient for the third Te site favorably agrees with the one expected for the I_{Te}:3Ga,1V site, we correspondingly suggest that this set of parameters must be associated with the $Te(I)_{As}$-V_{Ga} defect complex. For these processing conditions selected, indeed, a most abundant formation of Te_{As}-V_{Ga} pairs can be expected. As a result of the 10^{16} atoms/cm^2 implantation, the highest amount of residual damage will be formed, which, according to the amphoteric defect theory, after annealing will result in a preferential formation of gallium vacancies. High-energy fluence laser irradiations were shown to increase the amount of GaAs elementary point defects.[29–31] For the Au/Te/Au/GaAs system under study, this was confirmed by Raman and photoluminescence measurements.[28] Hence, for the highest-energy fluence irradiation conditions applied (2.5 and 0.85 J/cm^2), a relaxation away from the metastable quenched-in regime (characterized by a metastable high Te_{As} donor concentration, see Table I) towards a condition characterized by a large amount of Ga vacancies again can be expected. As mentioned previously, a pairing of the positively charged Te_{As} donor atoms with the negatively ionized V_{Ga} acceptors, stabilized by the Coulomb interaction, will occur.[1,2,8,13] The close similarity in the ^{129}I hyperfine interaction parameters attributed to the Te(I) DX center and to the $Te(I)_{As}$-V_{Ga} defect most consistently can be interpreted in view of the DX model proposed by Chadi and Chang.[32] According to these authors, a column-VI donor DX formation should be accompanied by a large lattice relaxation, including a bond rupturing of one of the (Te) nearest-neighbor Ga atoms, which is pushed to an interstitial site, leaving the donor atom threefold coordinated.

Hence, according to the above developed argumentation, similar field gradients can be expected for both the Te(I)-DX and Te(I)$_{As}$-V_{Ga} defects.

From our experiments, no information on the actual charge state of the Te(I)$_{As}$-V_{Ga} defect can be deduced. The conservation of the Te-parent charge state following the β^- decay of solid-state-embedded Te to I is neither guaranteed nor excluded.[20,21] Electrical measurements correlated to the Mössbauer results probably can help to provide a way out of this dichotomy.[33]

In conclusion, from a comparative study of the ^{129}I Mössbauer data on Ga_2Te_3, and Te-doped GaAs, we have found firm evidence for the identification of nearest-neighbor–vacancy-associated Te sites in GaAs. This result is in agreement with recent theories on the formation of donor-related defects in GaAs. It also provides an indication for the identification of the low resistance Ohmic conduction mechanism obtained on n- and p-type GaAs by identical (laser) processing conditions.[17]

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