IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Mossbauer spectra and the DX-centre complex in AlGaAs

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 5171

(http://iopscience.iop.org/0953-8984/1/31/016)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.93
The article was downloaded on 10/05/2010 at 18:33

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 1 (1989) 5171–5177. Printed in the UK

Mössbauer spectra and the DX-centre complex in AlGaAs

J A Van Vechten
Center for Advanced Materials Research, Department of Electrical and Computer Engineering, Oregon State University, Corvallis, Oregon 97331, USA

Received 15 December 1988

Abstract. Mössbauer spectra for the 'DX' deep-level defect in AlGaAs alloys are just now being made available—for example, in a recent article by Gibart and co-workers. The interpretation of these spectra has been somewhat clouded by the fact that Mössbauer specialists have generally not considered the anti-site defect among the defect complexes present in III–V crystals near the Mössbauer isotope that affect the various components of the spectra. We note that the anti-site defect is well established as a component of, for example, the EL2 deep-level defect, and generally as the most prevalent native point defect in III–V crystals. Furthermore, the spectra reported by Gibart and co-workers are consistent with the model wherein the 'X' of the DX defect complex is the pair composed of a metal-on-As-site anti-site defect plus a Ga vacancy that results from As vacancy nearest-neighbour hopping. In particular, they show that a major fraction of donors remain in an unperturbed state when DX compensates the sample.

The 'DX' phenomenon in AlGaAs alloys, and some other semiconductors, is a spontaneous compensation of all types of n-type doping at low temperatures that may temporarily be suppressed by absorption of sub-band-gap light (Lang and Logan 1977, Lang *et al* 1979, Lang 1985, Gibart *et al* 1988). The transition between the stable, largely non-conducting state and the metastable, conducting state has been attributed by some to a 'large lattice relaxation' (LLR) and by others to a mainly electronic relaxation. The origin of this low-temperature compensation effect and the 'persistent photoconductive transition' has been the subject of extensive investigation and controversy. The subject has practical import because it is widely believed that AlGaAs and similar semiconductors can compete successfully against Si only if they can be made to operate at temperatures (T) below the freeze-out temperature of acceptors in Si.

The earliest hypothesis (Lang *et al* 1979) was that the donors, D, tend to form complexes with a native point defect, X, which was proposed to be the As vacancy, $V_{As} = X$, and that X had two configurations connected by an unspecified LLR. At high T and in the metastable conductive state at low T, X was proposed to be neutral, so as not to compensate the doping and as is consistent with the usual attribution of deep-donor properties to V_{As}. Lang *et al* (1979) assumed that D remained a shallow donor while the complex became neutral via the LLR. This implies that the X changes from being neutral to being negatively charged in n-type material, i.e. that the LLR converts the deep donor to a deep acceptor, and this serves to compensate the sample to a large

degree. Van Vechten (1985) argued that this proposal is correct as far as it goes and that the LLR is simply nearest-neighbour hopping;

$$D^+ \, V^0_{As} + 3e^-_c \leftrightarrow D^+ \, M^{2-}_{As} V^-_{Ga} \qquad (1)$$

where e^-_c denotes an electron in the conduction band and M may be either Al or Ga, one of the nearest neighbours to the V_{As} that hopped in the reaction.

There have been several other origins proposed for the DX phenomenon. (The literature is so extensive that space does not permit one to do justice to all authors. Please consult the review by Lang (1985) and the paper of Gibart *et al* (1988).) We divide these into three classes: (i) there is no X and there is no LLR but there is a mainly electronic reconfiguration of the isolated donor giving rise to the two states; (ii) there is no X but the isolated donor undergoes a LLR itself; (iii) there is a LLR and an X but the LLR is not reaction (1) and X is not the V_{As}.

Before distinguishing between (1) and the three classes of alternatives, let us note that all proposed explanations must be similar in one respect that is not always appreciated. In order to account for any self-compensation effect that appears as a function of T, alloy composition, and pressure, one must consider the balance of free energies between the conducting and non-conducting states (Van Vechten 1980). For all proposals, there must be some cost of enthalpy to create the states that trap the carriers and this cost is paid back by the free energy released when carriers fall from the Fermi sea into these states. That free energy is a function of T, alloy composition, and pressure. Now, the observation of DX behaviour in pure GaAs under pressure (Mizuta *et al* 1985), when it is not found at 1 atm, has sometimes been claimed to prove there is no X. This would only be valid if one could also show there were not sufficient X in pure GaAs. In fact, positron annihilation studies (Dannefaer and Kerr 1986) show there are more than sufficient vacancies in all types of GaAs to account for the observed, high-pressure DX behaviour if (1) is the actual mechanism. Moreover, Theis *et al* (1988) have shown that the DX centre is present in unalloyed GaAs, but that it there has its ionisation level above the conduction band minimum, so the level can be occupied and the DX phenomenon can be 'observed' only by hot or highly degenerate electrons. For all proposals, the increase in the GaAs band gap with pressure increases the payback of trapping the carriers once the deep levels have been created to the point that, at sufficient pressure, the compensation reaction becomes favourable, as it is in the alloy. Moreover, the observed insensitivity of the DX phenomenon to the preparation of the sample does not serve to distinguish between alternatives; if, for example, one varies the As overpressure by a factor of ten during growth, then one could indeed vary the equilibrium concentration of neutral V_{As}, $[V^0_{As}]$, by a factor of 10, but not $[(V_M M_{As})^{-3}]$, which is a function not only of $[V^0_{As}]$ but also of the Fermi level, E_F. A shift of E_F by only $(kT/3)\ln 10 = 0.768\, kT$ would compensate this (large) variation of the vapour pressure and probably never be noticed.

We now consider the attributes of reaction (1) and compare and contrast them with the three classes of alternatives.

First, equation (1) implies that in the non-conducting state most of the donors are undistorted and isolated, i.e. unpaired from X. All the D would be compensated if there are a third as many V_{As} performing (1) as there are D. Also, the V_{As} do not need to be near any D to affect the compensation. As assumed implicitly by Lang *et al* (1979), there is a tendency for the V^0_{As} to pair with the D^+ in well annealed samples, but the attraction is not strong. It derives from the Coulomb attraction of the right-hand-side configuration in (1), which is not the preferred configuration at diffusion-processing temperatures, for

the D^+. Also the weaker binding between the D and the host atoms, which are its nearest neighbours, allows them to hop away more easily than can host atoms bonded to the other host atoms, so the vacancy tends to move toward the donor impurity. Indeed, Mössbauer studies of ^{119}Sn-implanted GaAs (Weyer *et al* 1980, Bonde-Nielsen *et al* 1985) identify a configuration of the Sn Mössbauer isotope with an isomer shift (IS) of 2.8 mm s^{-1}, as contrasted with the 1.8 mm s^{-1} IS of the isolated Sn_{Ga} and the 1.9 mm s^{-1} IS of isolated Sn_{As}, as the Sn_{Ga}–V_{As} nearest-neighbour complex, and find that this can be dispersed by quenching the sample from temperatures as low as the 200–300 °C range. Class (ii) alternative theories require every D that participates in the DX phenomenon, more than 95% for alloys with 24% to 74% Al, to be in the distorted configuration while class (i) theories require that none of the D be distorted. Class (iii) alternatives are not clear as to what they predict but they generally imply a coupling between each D participating and its particular X.

Second, equation (1) implies the 'DX' ought not to be a unique complex, but should be a family of related complexes This is because vacancy diffusion in III–V crystals occurs largely via nearest-neighbour hopping, which requires the formation of pairs of anti-site defects and results in a distribution of these normally neutral dipolar defects about the vacancy complexes (Van Vechten 1975, 1980, 1982, 1984, Van Vechten and Wager 1985, Juang *et al* 1988). Indeed, Bonde-Nielsen *et al* (1985) remarked that their studies of the Sn_{Ga}–V_{As} complex found a distribution in electric field gradients that indicates that the complex is not unique, but is subject to disorder. Class (i) and (ii) alternatives assert that D is isolated and imply a unique configuration for both states. Class (iii) proposals are either based on observations leading to the conclusion that DX is a family of complexes (Farmer *et al* 1988) or might imply this for similar reasons. An exception would be the hypothesis that X is a divacancy (Wager 1988), because divacancies migrate mainly by passing one atom across their two sites, which does not result in anti-site defect pair formation.

Third, equation (1) implies that the fraction (about a third or less) of conductive state donors that are paired with X will be in the field of a threefold ionised acceptor in the non-conducting states. Class (i) and (ii) alternatives assert the defect to be neutral, or at most singly ionised, in the non-conducting state. The class (iii) alternative of Wager (1988) asserts DX to be neutral; Farmer *et al* (1988) do not deal with the topic.

Fourth, for the case of Sn_{III} doping, which was used for the recent Mössbauer experiments (Gibart *et al* 1988) that we discuss, it follows that equation (1) implies the corresponding IS will be relatively large. Accurate and reliable *ab initio* IS calculations are available only for perfect substitutional sites (Svane 1988) but trends can be estimated with the aid of empirical identifications (Shenoy and Wagner 1978, Bonde-Nielsen *et al* 1985, Williamson 1986, Williamson *et al* 1987). It is well established that the IS is directly proportional to the electron density at the nucleus of the Mössbauer isotope—so, for example, the difference of the ISS between Sn_{Ga} and Sn_{As}, 1.8 as against 1.9 mm s^{-1}, corresponds to the charge transfer between these two sites imposed by the partly ionic character of GaAs. The IS = 2.8 mm s^{-1} identified with Sn_{Ga}–V^0_{As} in GaAs is attributed to the redistribution of charge from the bonds dangling into the vacancy cavity, mainly to the nearest neighbours and largely to states that overlap their core much more than do covalent bonds. It seems that those engaged in the identification of Mössbauer lines with defects have previously not considered anti-site defects among possible candidates, despite the firm establishment of their prevalence in III–V materials and participation in other metastable deep-level defects such as EL2 in GaAs and M in InP. (cf, e.g., Van Vechten 1980, Wager and Van Vechten 1987, Juang *et al* 1988, and many references

Table 1. Values of the fractional percentage resonance intensity, F, and of the isomer shift, IS, for samples of various mole fractions of Al content, x. The uncertainty of F is indicated in parentheses. The values are quoted from Gibart *et al* (1988).

Line \ x	0.0	0.20	0.30	0.40	0.43	0.70	0.76	1.00
1 F	73(3)	75(4)	40(7)	42(5)	50(4)	65(6)	67(5)	69(5)
IS	1.78	1.78	1.81	1.89	1.74	1.76	1.81	1.75
2 F	17(3)	14(3)	28(7)	24(11)	28(4)	14(8)	21(6)	17(6)
IS	2.5	2.22	2.39	2.57	2.26	2.38	2.47	2.53
3 F	10(3)	11(3)	32(7)	34(11)	22(3)	21(5)	12(3)	14(3)
IS	3.30	3.26	2.94	3.05	3.02	3.02	3.57	3.48

therein.) While a shallow impurity (dopant) in the vicinity of the Mössbauer isotope would have small effect on the IS due to the broad hydrogenic orbit of the carrier that they bind, deep levels such as the Ga_{As}^{2-} must make a significant contribution by binding two electrons in a highly localised state that would be a nearest neighbour to a Sn_{Ga} donor if (1) occurs from a V_{As} paired with it. The V_{Ga}^{-} deep level on the second-neighbour site of the Sn_{Ga} should also contribute. Thus, we expect the IS for Sn_{Ga}^{+}–M_{As}^{2-}–V_{Ga}^{-} to be even larger than that identified for Sn_{Ga}^{+}–V_{As}^{0}, about 3.1 mm s^{-1} judging by the trend cited. We note that the only previously identified source of an IS > 3.0 mm s^{-1} for ^{119}Sn in GaAs is the Sn interstitial produced by the decay of ^{119}Cd which gives IS $= 3.4$ mm s^{-1} (Bonde-Nielsen *et al* 1985). Interstitial Sn is highly unstable due to its very high enthalpy of formation, which results from the same large overlap of the host-bond charge density with its core (Van Vechten 1980), and almost certainly results from the 20 eV recoil energy of the Cd decay.

Reaction (1) also implies that the fraction of Sn donors that are paired with the vacancy–anti-site complex are in the presence of a strong electric field gradient which should produce a significant quadrupole splitting of the Mössbauer resonance. The author is not aware of an acurate method to estimate the magnitude of this quadrupole splitting of the IS and thus to predict whether or not it should be resolved experimentally.

Fifth, equation (1) implies the net charge of the DX complex in the non-conductive state to be -2. As the D^{+} is either first or second neighbour to the V_{Ga}^{-} for the majority of cases in well annealed samples, spin pairing is expected. Thus, for the type of sample generally investigated, the DX complex should have no unpaired spin and should be paramagnetically inactive. Class (i), (ii) and (iii) alternatives generally imply DX should be EPR-active in the non-conductive state; however, there are a few exceptions.

We now consider the Mössbauer data recently reported by Gibart *et al* (1988), who concluded that the spectra imply LLR (contradicting class (i) alternatives) but did not express a view on what they imply regarding anti-site defects, vacancies, etc (Mooney *et al* (1988) also affirm the presence of LLR).

The samples were an alloy series of metal–organic vapour-phase epitaxially (MOVPE) grown layers ranging from pure GaAs to pure AlAs doped during growth with ^{119}Sn. Thus, there was no ion implantation and no transmutation of the Mössbauer isotope. All measurements were at $T = 76$ K in the dark so that samples with Al mole fraction, x, between 0.25 and 0.75 must have been in the non-conductive state. Three Mössbauer lines were noted and traced through the alloy series. Table 1 reproduces relevant data. The variation of IS with x is moderately greater than experimental uncertainty, which is greatest (0.2 mm s^{-1}) for line 2 at $x = 0.2$ and is typically 0.1 m s^{-1} or better. The

Table 2. Analysis of the Mössbauer data of Gibart *et al* (1988) according to their assumption that DX appears in both line 2 and line 3, and according to our proposal that it contributes only to line 3.

x	0	0.20	0.30	0.40	0.43	0.70	0.76	1.00
$F_1(x) - F_1(0)$	0	2	−33	−31	−23	−8	−6	−4
$F_2(x) - F_2(0)$	0	−3	11	7	11	−3	4	0
$F_3(x) - F_3(0)$	0	1	22	24	12	11	2	4
[DX]/[D] (%)	0	−2.7	45	42	31	11	8.2	5.5
[DX]/[D]* (%)	0	1.34	30.1	32.9	16.4	15.1	2.7	5.5

intensity, F, of line 1 (Sn_{III}) and of line 3 vary with x much more than does that of line 2. For GaAs Williamson (1986) and Williamson *et al* (1987) identified line 2 with neutral Sn agglomeration (probably an artefact of the growth process, e.g., balling of Sn on the sample surface), and also proposed that line 3 and line 2 form a quadrupole doublet in pure GaAs. However, one might not expect to resolve the doublet if disorder broadening is as severe as Bonde-Nielsen *et al* (1985) found. In any case a quadrupole doublet would have to maintain a fixed ratio, which is generally expected to be 1.0, of intensity from one sample to the next. (Agglomerations of the dopant element cannot participate in the DX phenomenon but they cannot be eliminated from the observed spectrum either.)

The third line appeared weakly with an IS about as large as that of the Sn interstitial in the $x = 0$ and $x = 1$ samples, where DX behaviour is not evident unless hot electrons are injected, or the doping is highly degenerate, or pressure of order 20 kbar is applied. Note that Sn interstitials are not expected as there was no transmutation recoil nor any ion implantation to produce them. In the range of x where DX behaviour is dominant, roughly $0.24 < x < 0.74$, line 3 is second in strength and displayed an IS of about 3.1 mm s^{-1}. Gibart *et al* (1988) suggest that DX appears as a doublet, part of both lines 2 and 3, the remainder being the Sn agglomerations. We question this suggestion because the F-ratio does not appear to be constant and because there is evidence for disorder about DX from Farmer *et al* (1988). Alternatively, we suggest: (a) doublets are not resolved here; (b) line 2 alone results from agglomerations only; and (c) line 3 results from complexes based on Sn_{III}–$V_{As} \leftrightarrow Sn_{III}$–$III_{As}$–$V_{III}$, which are expected to occur also for alloy compositions where the DX transition is not favoured (Van Vechten 1985).

It is plain that, if we take F for line 3 alone to be DX, these data agree with (1) on the first point; in the range of the DX phenomena there are roughly twice as many isolated Sn_M normal donors as 'DX complexes' in the non-conducting state. The conclusion that the non-conducting state still has a majority of donors in their normal (shallow) configuration, thus implying that the DX complexes must be multiple acceptors, is also in accord with recent FTIR studies (Murray *et al* 1988) and with EXAFS studies (Mizuta and Kitano 1988).

If, on the other hand, we assume that Gibart *et al* (1988) are correct that DX appears as a doublet, part of both lines 2 and 3 which also contain contributions from Sn agglomeration, then we should analyse the data as in table 2. There we show the intensities of the three lines relative to their values in unalloyed GaAs, $F_i(x) - F_i(0)$, for the various values of x, the mole fraction of AlAs in the alloy, and then calculate the ratio of DX centres to total donors from

$$[DX]/[D] = [(F_2(x) - F_2(0)) + (F_3 - F_3(0))]/F_1(0). \quad (2)$$

For completeness and comparison, we also show the ratio of the concentration of DX

centres to total donors calculated according to our suggestion that DX contributes only to line 3, where its quadrupole splitting is unresolved;

$$[\mathrm{DX}][\mathrm{D}]^* = (F_3(x) - F_3(0))/F_1(0). \tag{3}$$

It seems safe to assume that the true situation lies between these two propositions.

For the four samples wherein the DX is expected to appear ($x = 0.30, 0.40, 0.43$ and 0.70), equation (2) yields an average empirical value of 32%, compared with the value of $\leqslant 33\%$ implied by (1), while (3) yields an average empirical value of 24%. It must be admitted that for the $x = 0.30$ and 0.40 samples, equation (2) could also be used to support the model of Chadi and Chang (1988), wherein the DX phenomenon is a negative-U behaviour of the isolated donors themselves:

$$\mathrm{D}^+ + 2\mathrm{e}^- \leftrightarrow \mathrm{D}^-. \tag{4}$$

This would imply that the ratio should be 50%. Among other reasons, we find the Chadi–Chang model difficult to accept because the DX phenomenon occurs for all donors, whether they reside on the anion or in the cation lattice site, at the same concentrations, Fermi level position, temperature etc. In any case it is plain that Mössbauer data are consistent with (1) regarding the third point.

As regards the second point, these Mössbauer data are also in accord with (1) in that they indicate disorder broadening of the DX complex line, as expected for a vacancy-related complex and as previously found by Bonde-Nielsen *et al* (1985) for the $\mathrm{Sn_{Ga}}$–$\mathrm{V_{As}}$ complex in GaAs. There are several other experiments that indicate that DX is not a single defect but is a family of related defects. These include the sample dependence of the DLTS spectra of DX transitions reported by Farmer *et al* (1988) and the studies of DX transition parameters in unalloyed GaAs under pressure by Mizuta *et al* (1985). These observations argue strongly against class (i) and class (ii) alternatives. It must also be remarked that phonon scattering studies by Narayanamurti *et al* (1979) gave early and persuasive evidence for the conclusion that $\mathrm{X} = \mathrm{V_{As}}$ in the conductive state.

Finally, regarding the fifth point, one can only say that despite a great deal of searching, no paramagnetic active centre has been found that could be ascribed to the DX complex (Weber 1988). This is in accord with (1) and contradicts many alternatives.

Acknowledgments

We acknowledge the partial support by the U S Air Force Office of Scientific Research (AFOSR 86-0309). Discussion of the Mössbauer effect and data with D L Williamson are gratefully acknowledged.

References

Bonde-Nielsen K, Grunn H, Haas H, Pedersen F T and Weyer G 1985 *J. Electron. Mater.* **14a** 1065
Chadi D J and Chang K J 1988 *Phys. Rev. Lett.* **61** 873
Dannefaer S and Kerr D 1986 *J. Appl. Phys.* **60** 591
Farmer J W, Hjalmarson H P and Samara G 1988 *Mater. Res. Soc. Symp. Proc.* **104** 585
Gibart P, Williamson D L, El Jani B and Basmaji P 1988 *Phys. Rev.* B **38** 1885
Juang M T, Wager J F and Van Vechten J A 1988 *J. Electrochem. Soc.* **135** 2023
Lang D V and Logan R A 1977 *Phys. Rev. Lett.* **39** 635
Lang D V, Logan R A and Jaros M 1979 *Phys. Rev.* B **19** 1015

Lang D V 1985 *Deep Centers in Semiconductors* ed. S T Pantelides (New York: Gordon and Beach) p 489
Mizuta M and Kitano T 1988 *Appl. Phys. Lett.* **52** 126
Mizuta M, Tachikawa M, Kukimoto H and Minomura S 1985 *Japan. J. Appl. Phys.* **24** L143
Mooney P M, Northrop G A, Morgan T N and Grimmeiss H G 1988 *Phys. Rev.* B **37** 8298
Murray R, Newman R C and Nandhra P S 1988 *Mater. Res. Soc. Symp. Proc.* **104** 543
Narayanamurti V, Logan R A and Chin M A 1979 *Phys. Rev. Lett.* **43** 1536
Shenoy G K and Wagner F E *Mössbauer Isomer Shifts* (Amstrdam: North-Holland)
Svane A 1988 *Phys. Rev. Lett.* **60** 2693
Theis T N, Mooney P M and Wright S L 1988 *Phys. Rev. Lett.* **60** 361
Van Vechten J A 1975 *J. Electrochem. Soc.* **122** 423
—— 1980 *Handbook on Semiconductors* vol 3, ed. S P Keller (Amsterdam: North-Holland) p 1
—— 1982 *J. Appl. Phys.* **53** 7082
—— 1984 *J. Phys. C: Solid State Phys.* **17** L933
—— 1985 *Mater. Res. Soc. Symp. Proc.* **46** 83
Van Vechten J A and Wager J F 1985 *Phys. Rev.* B **32** 5259
Wager J F 1988 unpublished
Wager J F and Van Vechten J A 1987 *Phys. Rev.* B **35** 2330
Weber E R 1988 unpublished
Weyer G, Damgaard S, Petersen J W and Heinemeier J 1980 *J. Phys. C: Solid State Phys.* **13** L181
Williamson D L 1986 *J. Appl. Phys.* **60** 3466
Williamson D L, Gibart P, El Jani B and N'Guessan K 1987 *J. Appl. Phys.* **62** 1739