Defects in GaAs

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Abstract. A comprehensive review of defects in GaAs with focus on native point defects and dislocations is given. The effects of these defects on devices are also considered. It is pointed out that a unified point defect model cannot at present be drawn from the available information. The importance of including anti-site defects in the point defect models which have hitherto only considered vacancies and interstitials is stressed. Attention is drawn to the need for understanding the dominant equilibrium native defects in GaAs both from fundamental and technological considerations. In this respect new experimental techniques are suggested to understand and control the defect structure. The current understanding of dislocations in GaAs is very much in its infancy compared to that in elemental semiconductors. Both theoretical work and careful experiments are wanting. This is essential since dislocations have been directly implicated in the degradation of GaAs devices.

Keywords. Native defects ; dislocations ; device degradation.

1. Introduction

Next to Si, GaAs is the most important semiconducting material today. GaAs and related compounds such as (Ga, Al) As and Ga (As, P) have received considerable attention in recent years because of their many potential applications. These applications include microwave devices, solar cells and several optoelectronic devices like light emitting diodes (LEDs), lasers, optoisolators, etc. With the refinements in crystal growth techniques, especially in epitaxial techniques which facilitate growing thin layers, the importance of this material has become more pronounced. As the demand for the material grew so did the demand for "perfect" material. More often than not poor devices result from poor starting material and the quality of the material is generally determined by the crystalline imperfections, which are invariably present. It has been the fond hope of both material scientists and device technologists to understand these imperfections and if possible to control them.

Crystalline imperfections include point defects, dislocations, stacking faults, grain boundaries, interfaces, etc. Foreign impurities are generally intentionally added to

the material during crystal growth to obtain desired electrical properties. For example, in GaAs the group VI impurities — S, Se, Te—are used to achieve *n*-type conductivity while group II impurities — Be, Mg, Zn — are used to get *p*-type conductivity. Even when the material is grown intentionally “undoped,” satellite impurities such as C, Si are present due to contamination from graphite crucibles and quartz containers used for crystal growth. As a result nominally undoped GaAs is never pure. Besides foreign impurities, point defects also include native defects which are vacancies (lattice sites empty of atoms), interstitials (atoms present at non-substitutional positions) and antisite defects (misplaced atoms). Thus for GaAs one can speak of V_{Ga} , V_{As} , Ga_i , Ga_{As} and As_{Ga} , where V_{Ga} is a vacancy at a gallium site, Ga_i is Ga atom occupying an interstitial site and Ga_{As} is Ga atom occupying an arsenic site and so on.

Dislocations can be present in the as-grown material due to a variety of factors such as thermal stresses, excess point defects precipitating to form prismatic dislocation loops, etc. Dislocations are also introduced during the multifarious device processing steps like diffusion, ion implantation, sawing, polishing and so on. The presence of dislocations is, in general, harmful to the devices and often times the crystal grower aims to grow “low” dislocation density material. Apart from dislocations, two-dimensional defects such as stacking faults, grain boundaries and interfaces can also be present. For example, stacking faults are present in the as-grown material due to excess impurity atoms precipitating as “extrinsic” faults or introduced during processing steps such as diffusion and oxidation. Like dislocations, stacking faults also have deleterious effects on devices.

With the advancement in the growth of GaAs over the years, single crystal ingots of reasonable size are routinely grown such that grain boundaries are not problems any more. However, for some applications such as polycrystalline solar cells, grain boundary transistors, etc., grain boundaries play an important role.

For many device applications such as injection lasers and LEDs, GaAs is currently grown by epitaxial techniques. This has introduced another area of research namely understanding the interfaces of epitaxial layers. Another type of interface is that between the semiconductor and dielectric films (Si_3N_4 , SiO_2 , etc.) which are deposited on GaAs during processing.

Current research on defects in GaAs is focussed on all of these imperfection impurities, native point defects, dislocations, stacking faults, grain and interface boundaries—with the aim to understand their nature and origin and to eliminate or control their density in the crystals. A review of all these defects is a Herculean task even if it were to be only on GaAs. For the sake of limiting the size of this review, focus is centred on native point defects and dislocations. In § 2 we consider native point defects which is followed by § 3 on dislocations. Section 4 discusses the effects of point defects and dislocations on devices. Section 5 summarizes the status of current understanding of this two class of defects in GaAs. Attention is drawn to the need for new tools to explore the GaAs defect structure.

2. Native point defects

2.1 Definition

Native point defects in GaAs can exist on both sublattices. Besides vacancies and interstitials, (sometimes referred in literature as self-interstitials to distinguish

from foreign impurities occupying interstitial sites) in a compound AB , A atoms can occupy sites belonging to B atoms and *vice versa* giving rise to misplaced atoms (Kroger 1974 and Van Vechten 1975). Thus in GaAs, we have V_{As} , As_i and Ga_{As} in the As sublattice and V_{Ga} , Ga_i and As_{Ga} in the Ga-sublattice. These point defects can exist in neutral or charged form. The following notation has been proposed by Kroger and Vink (1956) to denote the charge state of the point defects; x denotes a neutral defect, prime denotes a defect with a negative charge and a dot denotes a defect with a positive charge. Thus V_{Ga}'' is a doubly negatively charged gallium vacancy. The symbols used above actually represent effective charges rather actual charges of the defects. The difference in the charge states of a crystal site with and without an imperfection is defined as the effective charge. This distinction does not, however, apply for interstitial defects where the actual and effective charges are the same.

While the single substitutional defects — V_{Ga} , As_{Ga} , V_{As} , Ga_{As} — retain T_d symmetry in their unrelaxed positions, the symmetry of the interstitial defect depends on the particular configuration. The interstitial has the T_d symmetry only if it occupies the centre of the unit cell (figure 1). In this configuration the interstitial is in an essentially nonbonding site. The interstitial can also exist in a bonded configuration. For example, a Ga_i' defect can nestle between a Ga and an As atom and form bonds with its two valence electrons in the bond-centred configuration. A third configuration is the split-interstitial configuration where two atoms occupy the same substitutional site. These three interstitial configurations are shown in figure 1. For a discussion of these interstitials in Si, see the review by Corbett and Bourgoin (1975).

At present, no theoretical or experimental discussion of the different interstitial sites in GaAs exists. Of the three configurations one might expect the *bond-centred* configuration to be the likely one for small impurity interstitials such as b_i'' and *body-centred* one for the self-interstitials. But in both diamond and silicon, theoretical calculations suggest that the split $\langle 100 \rangle$ interstitial is the lowest energy configuration for neutral as well as singly positively and singly negatively charged self-interstitial (Corbett and Bourgoin 1975). In view of some of the current point defect models in GaAs (Hurle 1979) which suggest interstitial defects to be one of the dominant native defects under equilibrium conditions both theoretical and experimental investigations of interstitials in GaAs would hopefully be initiated.

Besides single point defects, defect clusters would also occur. Such higher order defects would be particularly important in GaAs which is subjected to some radiation damage *e.g.* ion-implantation. Two examples for defect clusters are a divacancy $[(V_{\text{Ga}})_2 \text{ or } (V_{\text{As}})_2]$ and prismatic dislocation loop which is formed as the result of aggregation of a large number of vacancies or interstitials.

2.2 Charged point defects

As we noted in the earlier section point defects can exist in either neutral or charged form. It is *a priori* difficult to predict what one should expect for the charge state

Figure 1. Interstitial configurations in GaAs: (a) tetrahedral configuration (b) bond - centered configuration (c) $\langle 100 \rangle$ split interstitial configuration (Corbett and Bourgoin 1975).

of a particular imperfection. Moreover, the charge state of the defect need not be the same under all conditions. For example, a vacancy in Si is known to exist in four forms— $V^{\times}$, $V^{\cdot}$, V' and V'' —as $V^{\cdot}$ in p -type Si and as V' and V'' in n -type Si (Watkins 1975). Further recent refined theoretical calculations which take into account the lattice relaxation near the vacancy (Baraff *et al* 1980) showed that in p -type Si, a doubly positively ionized vacancy, V'' , has a stable level in the forbidden gap and that $V^{\times}$, $V^{\cdot}$ and V'' form an "Andersen negative - U " system. That is, the energy level of V'' is in fact above that of $V^{\cdot}$ due to the large Jahn-Teller

relaxation energy associated with V^x . In other words $V^{\cdot}$ is a metastable state and it would transform into V^x and $V^{\cdot\cdot}$. Experimental results confirm this hypothesis (Watkins and Troxell 1980).

The understanding of point defects in GaAs is very much in its infancy compared to Si. Both theoretical calculations and careful experiments are wanting. Notwithstanding these difficulties it is perhaps helpful to adopt certain general rules (Kroger 1974) regarding the charge state of the point defects in GaAs.

- (i) Misplaced atoms — As_{Ga} , Ga_{As} — would be expected to behave in the same way as a pentavalent impurity on a Ga site or a trivalent impurity on an As site. That is, As_{Ga} would behave as a doubly ionizable donor and Ga_{As} would behave as a doubly ionizable acceptor.
- (ii) Interstitial atoms act as donors when their outer electron shell is less than half-full and as acceptors in the opposite case. Thus Ga_i would behave as a donor and As_i would behave as an acceptor in the tetrahedral sites.
- (iii) Vacancies have donor action if the number of unpaired electrons near the vacancy is less than half the number of valence electrons present near the same site in the absence of vacancies. The opposite is true for the acceptor vacancy. Thus V_{Ga} would behave as an acceptor and V_{As} would behave as a donor.

2.3 Defect chemistry

Native defects are introduced in GaAs when it is grown or when it is annealed after growth at high temperature and at some suitable partial pressure of one of the constituents, namely As in this case. After growth or annealing, when the crystals are somewhat rapidly cooled to room temperature, the high temperature equilibrium of native point defects is assumed to be frozen in. The concentration of point defects are then calculated by formulating quasi-chemical reactions involving the structure elements of the defects and atoms or molecules in outer phases and using the laws of mass action (Kroger 1974). The quasi-chemical approach is very helpful to calculate the variation in the concentration of point defects as a function of temperature and/or partial pressures of the dopants or one of the constituents of the compound and later compare the results with experimental data.

When defect calculations are performed some assumptions are made about the dominant native atomic disorder. There are three basic disorder mechanisms applicable to GaAs involving imperfections of the same nature:

- (i) Schottky disorder involving V_{Ga} and V_{As} .
- (ii) Interstitial disorder involving Ga_i and As_i .
- (iii) Anti-structure disorder involving Ga_{As} and As_{Ga} .

In order to maintain the As/Ga site ratio required by the crystal structure, in a stoichiometric crystal the imperfections in (i), (ii), and (iii) occur in sets containing at least two types of them. Besides the three basic disorder mechanisms one can

Figure 2. Defect concentrations at 1473 K as a function of parameter R ($\propto P_{As_2}^{1/2}$). The quantities ΣV_{As} and V_{Ga} are shown together with the experimental values $[V_{As}]_{pp}$ and $[V_{Ga}]_{CD}$ (Logan and Hurle 1971).

have combinations of these. For example the Frenkel disorder involves V_{Ga} and Ga_i in the Ga-sublattice or V_{As} and As_i in the As-sublattice. Thus there are nine possible types of disorder in GaAs.

Logan and Hurle (1971) first calculated the equilibrium concentration of point defects in GaAs as a function of temperature and arsenic pressure using the quasi-chemical approach. They assumed Schottky disorder mechanism as the dominant one based on the experimental data of Potts and Pearson (1966) and Chakraverty and Dreyfus (1966) available then. The concentration of the defects at 1200°C ($0.98 T_M$ where T_M is the melting point in degrees Kelvin) calculated by Logan and Hurle as a function of a parameter which is proportional to $P_{As_2}^{1/2}$ is shown in figure 2. Note also that they have assumed that V_{As} behaves as a single donor and V_{Ga} as a single acceptor and that they have included $(V_{Ga})_2$ and $(V_{Ga})_2'$ in the analysis.

Precision lattice parameter and density measurements on samples prepared under varying conditions have, however, cast doubt on the assumption that Schottky disorder was dominant. Principally, the lattice parameter measurements (Driscoll *et al* 1971; Driscoll and Willoughby 1972) indicated that the lattice parameter increases after annealing at high arsenic pressures. Similarly the density measurements of Bublik *et al* (1973) showed that on As rich side there is an excess mass per unit cell. Both these measurements suggested the existence of As_i or As_{Ga} on the As rich side of GaAs. Based on this new data Hurle (1979) revised the earlier point defect model (Logan and Hurle 1971) by considering the Frenkel disorder in the As-sublattice (As_i , V_{As}) as the dominant disorder. Hurle (1979)

Table 1. Defect reactions and the corresponding mass action relations and estimated equilibrium constants for undoped GaAs (Hurle 1979)

(1)	$0 = e + h ; np = k_i$
(2)	$As_{As} + V_i = As_i^x + V_{As}^x ; [As_i] [V_{As}] = K_{fa}$
(3)	$As_i^x = As_i + e ; [As_i] n / [As_i^x] = K_{ai}$
(4)	$V_{As}^x = V_{As} + e ; [V_{As}] n / [V_{As}^x] = K_{av}$
(5)	$\frac{1}{2} As_2(g) + V_i = As_i^x ; [As_i^x] = K_{As_i} p_{As_2}^{1/2}$

(1)	$K_i = 1.00 \times 10^{-12} T^3 \exp (-1.52/kT)^a$
(2)	$K_{fa} = 2.92 \times 10^6 \exp (-4.85/kT)$
(3)	$K_{ai} = 4.9 \times 10^{-9} T^{3/2} \exp (- ? / kT)$
(4)	$K_{av} = 442 \exp \left(- \frac{0.27}{kT} \right)$
(5)	$K_{As_i} = 16.4 \exp (-1.13/kT)$

Hurle used 1.62 eV for E_q which is incorrect.

also considered the incorporation of Sn, Te and Ge in GaAs. Defect reactions and the estimated parameters of the corresponding mass-action constants considered by Hurle for undoped GaAs are given in table 1.

2.4 Experimental observation of point defects in GaAs

Since the physical properties are greatly affected by imperfections, a variety of experiments have been performed with the aim to understand the point defect structure. These include self-diffusion experiments, Hall measurements, optical measurements (infrared absorption and photoluminescence), transient capacitance measurements, lattice parameter and density measurements and internal friction measurements. Table 2 lists the techniques that have been used in GaAs with some appropriate references.

Of the techniques that have been used in GaAs, electrical (Hall and conductivity) measurements and photoluminescence measurements are the two which are mostly commonly employed. Ikoma and Wang (1969) and Ikoma (1970) made Hall measurements on undoped GaAs in the temperature range 300–900 K and observed that the measured carrier concentration above 600° K was much in excess of the intrinsic carrier concentration. By fitting the temperature dependent Hall

Table 2. Experiments performed to understand the defect structure of GaAs.

Experiment	References
1. Self-diffusion	Goldstein 1961, Palfrey and Willoughby 1980
2. Hall, conductivity	Chiang and Pearson 1975a, Ikoma 1970
3. Density	Bublik <i>et al</i> 1973
4. Lattice parameter	Driscoll and Willoughby 1972
5. Internal friction	Chakraverty and Drefyus 1966, Osvenskii, Kholodnyi and Milvidskii 1972
6. Deep level transient spectroscopy	Lang, Logan and Kimerling 1977
7. Photoluminescence	Williams and Bebb 1972
8. Electron Paramagnetic Resonance	Wagner <i>et al</i> 1980
9. Position lifetime	Gopinathan <i>et al</i> 1977
10. Ballistic phonon attenuation	Narayanamurti, Logan and Chin 1979
11. Mossbauer spectroscopy	Holm and Weyer 1980
12. Transmission Electron Microscopy	Narayanan and Kachare 1975

data these authors deduced in epitaxial GaAs an electron trap (10^{19} – 10^{20} cm $^{-3}$) with an activation energy of 0.25 eV above the valence band which was suggested to be a native defect. Hurle (1979) hypothesized this defect to be V_{As} acting as a donor. He, however, noted that the high density of V_{As} deduced by Ikoma and Wang was probably incorrect due to their omission in the analysis of the contribution from the substrates of the epitaxial wafers. Hurle (1979) further noted that in the high temperature Hall measurements of Roberts (1965) done in sealed ampoules with excess As, the observed intrinsic behaviour up to 1190°C was perhaps due to a low concentration of V_{As} and that As_i present under the experimental conditions were neutral. Based on the result that at high temperatures GaAs is extrinsic with the electron concentration probably equal to $[V_{As}]$, Hurle (1979) re-examined the solubility data for Te in GaAs in the light of his revised point defect model and deduced the ionization energy of V_{As} to be 0.27 eV (see table 1).

Chiang and Pearson (1975a) carried out high temperature annealing experiments under controlled arsenic pressures and observed that donors and acceptors are created by the treatments. The donor and acceptor were suggested to be V_{As} and V_{Ga} since their concentrations varied as $p_{As_4}^{-1/4}$ and $p_{As_4}^{1/4}$ respectively. Photoluminescence measurements made concomitant with electrical measurements (Chiang and Pearson 1975b) suggested that both V_{Ga} and V_{As} are nonradiative. Chiang and Pearson (1975a) also deduced from their results the ionization energies of V_{As} and V_{Ga} to be 0.7 and 0.4 eV respectively. This is at variance with the value used by Hurle (1979). Further, according to Hurle's model one would expect that the donor concentration at room temperature due to V_{As} should be high in undoped GaAs grown from Ga solution contrary to what is generally observed. For this

reason Hurle (1979) proposed that the V_{As} disappear from the crystal on cooling by precipitating out from solution at some internal sink or by forming Ga_{As} . Chiang and Pearson (1975a) on the other hand observed donor behaviour after the crystals were cooled to room temperature. However, their results are not beyond doubt (Kroger 1977).

The assignment of donor action to V_{As} in the above papers is consistent with theoretical calculations on vacancies in GaAs. The essence of all the theoretical calculations is as follows. When a neutral atom, say As, is removed from the otherwise perfect crystal, V_{As} that is formed is surrounded by the three electrons of the Ga atom. Similarly when V_{Ga} is formed, five of the As valence electrons are involved. The problem is then to find the electronic states that must be occupied by these "dangling" or unpaired electrons. The theoretical calculations that have been made so far, each following a slightly different approach arrive at the following result. There are two electronic states of a_1 and t_2 symmetry associated with a vacancy. For V_{Ga} which has 5 electrons, two are in a_1 state and the other three are in t_2 state. If spin degeneracy is included, the t_2 state can accept three more electrons and thus V_{Ga} acts as an acceptor. On the other hand the t_2 state of V_{As} is occupied by one electron and the remaining two electrons are in a_1 state. In this regard V_{As} acts as a donor. The energy levels of the donor and acceptor states, however, differ in these calculations. Il'in and Masterov (1976) obtained 0.25 eV below the conduction band for the V_{As} donor level and 0.3 eV above the valence band for the V_{Ga} acceptor level. Fazzio *et al* (1979) obtained 0.17 eV and 0.55 eV for the same defects. On the other hand Berholc and Pantelides (1978) and Jaros and Brand (1976) find the t_2 state of V_{As} to be slightly above and in resonance with the conduction band. It may be unrealistic to compare these theoretical calculations with experiments especially in view of the fact that the calculations have been made in the unrelaxed lattice without invoking effects of Jahn-Teller distortion. Such effects have been shown to have profound influence on the energy levels of vacancies in Si (Baraff *et al* 1980). Self-consistent calculations of the energy levels of vacancies in GaAs similar to those used for silicon vacancy (Baraff *et al* 1980) have recently been initiated (Bachelet *et al* 1981).

In a few experiments acceptor action of V_{As} has also been proposed. Munoz *et al* (1970) investigated the classic problem of type conversion observed in *n*-type GaAs when heat-treated at high temperatures (760° C) as a function of arsenic pressure and found that acceptors are created at both high and low arsenic pressure as shown in figure 3. They suggested that the acceptors are vacancies, V_{As} at low and V_{Ga} at high arsenic pressures respectively. Otsubo *et al* (1977) studied both bulk crystals and epitaxial films of GaAs annealed in an H_2 flow by photoluminescence technique. They observed a new band at 1.39 eV at 77° K after annealing. By noting that the amount of material near the surface which is damaged by annealing varies as the square root of heating time they concluded that diffusion limited process occurs at the heat-treated surface and V_{As} is the diffusing species. Further they suggested that the 1.39 eV band is a donor-acceptor transition where the acceptor is suggested to be V_{As} .

Ikoma and Nakagawa (1972) considered the incorporation of amphoteric impurities in GaAs grown by vapour phase epitaxial techniques within the frame-

Figure 3. Change in surface carrier concentration in a variety of LPE GaAs crystals as a function of As_4 pressure. Heat treatments were performed at 850°C for 30 min (Munoz *et al* 1970).

work of a model developed by Rytova and Fistul (1970) and found that the concentration of the compensating acceptors decreased with increasing partial pressure of arsenic. Therefore they suggested V_{As} to be the acceptors. Hasegawa and Majerfield (1976) associated a 0.64 eV hole trap above the valence band to V_{As} .

The assignment of acceptor behaviour to V_{As} is in apparent conflict with the result of Chiang and Pearson (1975a). Though V_{As} can be created under deficient As conditions the reasons given for the assignment of the acceptor to V_{As} in all these experiments are questionable. Ga_{As} is also one of the possible point defects created under low As pressure. This defect is expected to behave as a double acceptor and could very well be responsible for the type conversion. Further the role of Si_{As} , which is a shallow acceptor, in these experiments cannot be excluded. Si is a common contaminant even in undoped GaAs because growth furnaces invariably contain quartz tubes. Under low As pressure Si_{As} would be expected to form by the reaction of Si_{Ga} with V_{As} (Spitzer and Allred 1968).

The role of native defects in GaAs has been emphasized in several other experiments where impurity-vacancy complexes have been invoked to explain the results. Photoluminescence has been one of the principal tools used in studying native defect complexes. The peak position of the bands seen predominantly in photoluminescence measurements and the suggested defect assignments are listed in table 3. It is clear that a comprehensive defect picture cannot at present be drawn from the photoluminescence measurements alone as evidenced by the conflicting assignments of the same emission band to more than one defect. The principal reason for this is that the crystals used by the various researchers are not of the same quality. Also the assignment of emission bands to single point defects is

questionable as they are believed to be non-radiative. Chiang and Pearson (1975b) did not observe any new band assignable to vacancies after heat treatment. The decrease in photoluminescence intensity immediately following radiation damage is also believed to be due to the non-radiative nature of point defects (Arnold 1969; Jeong *et al* 1973; Swaminathan *et al* 1981b). Further, in annealing experiments the possibility of contamination by fast diffusing impurities such as Cu cannot entirely be ruled out.

Table 3. Peak positions of deep centre luminescence bands in eV and the suggested defect assignments in GaAs.

Peak position (eV) in the range				
0.5	0.8-1.0	1.2	1.34-1.37	1.39-1.41
0.58 $V_{Ga}^{(1)}$	0.81 $V_{Ga}^{(1)}$		1.34 $Sn-V_{As}^{(1)}$	$V_{As}^{(12)}$
	0.93 $(V_{Ga}V_{As})^2$	1.2 $D-V_{Ga}^{(5)}$	1.35 $V_{Ga}^{(1)}$	1.39 $D-V_{As}^{(13)}$
	1.02 $(V_{Ga}V_{As})^1$		1.35 $Cu-V_{As}^{(7)}$	1.41 $Si_{As}-V_{As}^{(14)}$
	1.0 $V_{Ga}^{(3)}$		1.36 $Si_{As}-V_{As}^{(8)}$	1.41 $C_{As}-V_{As}^{(15)}$
	1.0 $Si_{As}-V_{As}^{(4)}$		1.35 $V_{As}^{(9,10)}$	
	1.0 $Cu_{Ga}-V_{As}^{(2)}$		1.37 $Cu^{(1)}$	
			1.37 $Zn_{Ga}-V_{As}^{(11)}$	
			$Cd_{Ga}-V_{As}$	
			$Cu_{Ga}-V_{As}$	
			$Cu_{Ga}-D_{As}$	

1. Chang, Esaki and Tsu 1971	9. Kryukova <i>et al</i> 1974
2. Vorobkalo <i>et al</i> 1973 ; Brailovskii, Groza and Broudnyi 1973	10. Lin <i>et al</i> 1975
3. Pois and Pinard 1974	11. Hwang 1968, 1969
4. Batavin and Popova 1974	12. Romano, Moran and Ashley 1973
5. Williams and Bebb 1972	13. Otsuba <i>et al</i> 1977
6. Nishizawa, Sinozaki and Ishida 1973	14. Itoh and Takeuchi 1977
7. Glimchuk and Prokhorovich 1975	15. Lum <i>et al</i> 1977
8. Birey and Sites 1980	

Figure 4. (a) Excitation and emission spectra due to the localized V_{Ga} -donor complex in Ge-doped GaAs. (b) The one-electron configurational coordinate model for vacancy complexes in GaAs. Also shown is the bandgap, and donor-like (D) and acceptor-like (A) levels of the zero-point energies of the ground state and excited states, respectively, which lie within the gap. E_{abs} , the absorption energy, is greater than E_{ems} , the emission energy, and the difference is the Stokes shift. The electron transitions are vertical because of the Franck-Condon principle. ΔE is the activation energy for thermal quenching of the luminescence (Williams and Bebb 1972).

Of all the emission bands observed in GaAs, there is general consensus about the assignment of the 1.2 eV band to donor V_{Ga} complex. This band is seen in all donor-doped samples and is weak in solution-grown GaAs. The latter supports the role of V_{Ga} since its concentration is expected to be low in solution grown material. Other features of this band are that it is broad with typical band widths of 150–200 MeV (Williams and Bebb 1972), that it is well separated from the band edge and is weak compared to the near band edge luminescence, and that it shows a large Stokes shift (figure 4a). The configurational coordinate model is invoked to explain this emission which is thought to be a localized transition in a donor- V_{Ga} molecule whose excited state is derived from the donor and the ground state from V_{Ga} (figure 4b). Bands having similar emission features have been

observed in epitaxial $\text{Ga}_{1-x}\text{Al}_x\text{As}$ and impurity-vacancy complexes have been invoked. For example, a broad band observed at 1.55 eV in Ge-doped $\text{Ga}_{0.6}\text{Al}_{0.4}\text{As}$ grown by liquid phase epitaxy has been assigned to $\text{Ge}_{\text{As}}\text{-V}_{\text{As}}$ complex (Swaminathan *et al* 1981b). Several broad bands observed in Sn-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ grown by molecular beam epitaxy have been attributed to complexes involving Sn and V_{Ga} (Swaminathan and Tsang 1981c).

The emission band at 1.41 eV has been studied quite extensively since it is observed after heat treatment in GaAs substrate used for growing epitaxial layers (Swaminathan *et al* 1981d). This band has been attributed to $\text{Si}_{\text{As}}\text{-V}_{\text{As}}$ (table 3). The participation of Si in this band is clear since it is observed only in Si-doped GaAs and further Swaminathan *et al* (1981) while identifying this band as due to donor-to-acceptor pair transition estimated the ionization energy of the acceptor to be 35 MeV which is in agreement with the value for Si_{As} (Ashen *et al* 1975). The intensity of the band was found to decrease after As implantation (Itoh and Takeuchi 1977) and the band was absent after annealing under As-rich conditions (Rao and Duhamel 1978). Both these experiments suggested the role of a As deficient native defect— V_{As} — Ga_{As} or Ga_i — in the band. A difficulty in choosing V_{As} as the defect is the observation that the 1.41 eV band is much narrower (typical band widths 25-50 MeV (Swaminathan *et al* 1981d)), than the 1.2 eV band which has been assigned to donor- V_{Ga} complex. Since vacancy-related luminescence centres are expected to be broad and well separated from the band edge, as for example in the case of the 1.2 eV band, perhaps Ga_i or impurity complex involving Ga_i might be the donor in the 1.41 eV band (Swaminathan *et al* 1981d).

Impurity-vacancy complexes have also been invoked in other experiments. Hurle (1979) considered donor- V_{Ga} complexes as the compensating acceptors in Te and Sn doped GaAs and vapor grown Ge-doped GaAs (see also Kasano 1978). An electron trap at 0.83 eV below the conduction band which has been observed in GaAs grown by vapour phase epitaxy (Miller *et al* 1977; Bhattacharya *et al* 1980) has been suggested to involve V_{Ga} because of the linear dependence of the trap on As/Ga ratio. Swaminathan and Copley (1975b) investigated the role of $\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}}$ complexes in Si-doped GaAs and suggested the interaction between such complexes and mobile dislocations as being responsible for the hardening of GaAs containing donor impurities. The persistent photoconductivity observed in donor doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ has been suggested to arise from donor- V_{As} complexes (known as DX centres in literature) (Lang *et al* 1979; Lang and Logan 1979). A firm support for this assignment was obtained when different symmetries for the complex depending on whether the donor is on As-site or Ga-site were observed in measurements of attenuation of ballistic phonons (Narayanamurti *et al* 1979). A $\text{Te}_{\text{As}}\text{-V}_{\text{Ga}}$ complex having trigonal symmetry has been proposed in Te-doped GaAs from internal friction measurements (Osvenskii *et al* 1972).

The point defect structure in GaAs has also been investigated by studying the recovery of damage in samples which have been irradiated with some suitable high energy particles. We shall refer the reader to a recent review of this subject on III-V compounds (Lang 1976). Briefly, Lang *et al* (1977) investigated in detail by deep

Figure 5. Deep level transient spectroscopy spectrum of *n*-type GaAs irradiated at room temperature with 1 MeV electrons. Levels *A* and *B* are present before irradiation. Irradiation induced levels are the five electron traps E_1 to E_5 and one hole traps H_1 . The relative positions of the levels in the gap are shown in the inset on the right-hand side of the figure. Note the compressed scale for E_1 and E_2 and the expanded scale for E_4 and E_5 (Lang *et al* 1977).

level transient spectroscopy GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$ irradiated with 1 MeV electrons. They observed totally 6 energy levels, five electron traps and one hole trap after irradiation. The energy levels of these defects are shown in figure 5. The E_1 , E_2 and E_3 levels were attributed to simple native defects. By studying the variation of these energy levels as a function of x in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ they suggested the E_3 level to be due to V_{Ga} . This assignment was based on the observation that this level does not vary with x meaning that it is tied to the valence band *i.e.* V_{Ga} like behaviour. Recently, Pons *et al* (1980) have, however, disagreed with this assignment. They identified the E_2 level instead with the vacancy.

Indirect evidence for native defects and impurity vacancy complexes have also been provided by structural measurements in annealed GaAs by transmission electron microscope. Narayanan and Kachare (1975) investigated the microstructures of annealed heavily Si doped GaAs. They observed prismatic dislocation loops in samples annealed in the range 600 to 850° C after a high temperature anneal at 1100° C. They identified the prismatic loops to be of vacancy type. Based on the temperature dependence of the number and size of the loops they suggested $(\text{Si}_{\text{Ga}} - V_{\text{Ga}})$ complexes as the precursor defect to the vacancy loops. Prismatic loops observed in Li-diffused GaAs have also been identified to be vacancy type (Norris and Narayanan 1977).

Laister and Jenkins (1971) had earlier identified prismatic loops observed in annealed Te-doped GaAs to be vacancy type. Subsequently Hutchinson and

Dobson (1974, 1975a) Morgulis *et al* (1974) and Wagner (1977) concluded that the prismatic loops in Te-doped GaAs and epitaxial $\text{Ga}_{0.64}\text{Al}_{0.36}\text{As}$ (Wagner 1978) were actually of interstitial nature. While Morgulis *et al* assumed that the interstitial loops were formed by Te atoms, Hutchinson and Dobson suggested that they were formed by the native interstitials. Hutchinson and Dobson (1974) also found that after 1 MeV electron irradiation and a 450°C anneal the prismatic dislocation loops grew which they considered as a support for the interstitial nature of the loop. This argument is not tenable for two reasons. First, both interstitials and vacancies would be created by 1 MeV electron irradiation. Second, there has been no independent identification of interstitials even though vacancies have been attributed to the electron traps created by irradiation (Lang *et al* 1977; Pons *et al* 1980). Kamejima *et al* (1979) identified interstitial type prismatic loops in S-doped GaAs. Recently Hughes and Narayanan (1978) investigated Te-doped GaAs and disagreed with the interstitial identification of the prismatic loops and concluded that they were indeed vacancy type.

The resolution of this conflict between the vacancy and interstitial assignments of the prismatic dislocation loops observed in annealed GaAs is a crucial one. Hurle (1979) accepted the interstitial picture in developing the point defect model for Te-doped GaAs. The contrast analysis in the transmission electron microscope to determine whether a prismatic dislocation loop is interstitial type or vacancy type is unambiguous only when the loops are fairly large (loop diameter $> 50\text{\AA}$). In the above mentioned investigations the contrast analyses were performed on loops having diameter 100-500 $\text{\AA}$ or greater and therefore experimenters' error is perhaps not the reason for the different results. A plausible reason could be differences in the starting material and/or the different methods of preparation of the samples for the annealing treatments. For example, while Hughes and Narayanan (1978) cleaned their samples and the quartz tubes used for the annealing experiments in aqueous KCN solution to reduce possible Cu contamination such a procedure was not followed by Hutchinson and Dobson (1974, 1975a.). It is worthwhile to mention here that the controversy of vacancy type *versus* interstitial type prismatic dislocation loops also exists in another III-V compound viz. GaP. Prismatic loops in S-doped GaP were identified as vacancy type by Stacy and DeKock (1978) and as interstitial type by Umeno *et al* (1979) and Ball and Hutchinson (1980).

In majority of experiments and theories invoking native defects, the anti-site disorder has not been considered at all. Van Vechten (1975) has calculated the formation energy of antisite disorder to be 6.1 eV as compared to 5.2 eV for the Schottky disorder or 5.6 eV for the mixed antisite vacancy disorder. This suggests that the Schottky disorder might be more important than the antisite disorder. However, as we have noted earlier, the difficulty in assigning the acceptor created by heat-treating GaAs at low arsenic pressure to V_{As} , in disagreement with the expected donor action for it, could easily be resolved by supposing that the acceptor is Ga_{As} . Moreover, recently Wagner *et al* (1980) have shown by high-field electron paramagnetic resonance the presence of As_{Ga} . This new evidence necessitates the inclusion of antisite defects in the future point defect models.

Figure 6. (a) The cubic unit cell of GaAs. (b) Stacking of $\{111\}$ planes. (c) Projection of figure 7b on the $\{110\}$ plane (Alexander and Haasen 1968).

3. Dislocations

3.1 Perfect Dislocations

GaAs crystallizes in the zinc blende structure which can be described as two interpenetrating fcc lattices. One lattice which is occupied by Ga atoms is shifted by $a/4 [111]$ relative to the other fcc lattice, which is occupied by As atoms, a being the length of the fcc cube edge (figure 6a). The close packed $\{111\}$ planes of the fcc lattice become pairs of $\{111\}$ planes in GaAs as is shown in figure 6b or in a two-dimensional projection on the $\{110\}$ plane in figure 6c. Because of the presence of two type of atoms, there is a polarity in stacking of the $\{111\}$ planes. If $ABCABC$ is the stacking order of $\{111\}$ planes in the first fcc sublattice and $\alpha\beta\gamma\alpha\beta\gamma$ that in the second, then $\alpha B, \beta C, \gamma A$ are closely spaced pairs of planes connected by three times as many bonds as are between the three times wider spaced $A\alpha, B\beta, C\gamma$ pairs of planes.

Figure 7. (a) The GaAs structure with a $[111]$ direction vertical. A $\{111\}$ slip plane, the line direction and the Burgers vector of a 60° dislocation are shown. (b) The result of moving a 60° dislocation into the crystal from right to left is to produce the relative moments of the atoms indicated by the arrows. (c) The 60°

dislocation of the shuffle set in GaAs. $\vec{l}$ and $\vec{b}$ lie along $\langle 110 \rangle$ directions. The slip plane is of $\{111\}$ type (Holt 1962).

Hornstra (1958) first examined the structure of a complete dislocation in crystals with diamond cubic structure and later Holt (1962) extended the analysis to the zinc blende structure. The important types of dislocations are the 60° dislocation and the screw dislocation in the $\{111\}$ plane (60° is the angle between the dislocation line and the Burgers vector (figure 7). Haasen (1957) pointed out that there are two types of 60° dislocations in a compound semiconductor which he called α and β dislocations. The α dislocation in GaAs ends with a row of Ga atoms, while the β dislocation ends with a row of As atoms. The characteristics of complete dislocations having Burger's vector $a/2[110]$ are shown in table 4.

Table 4. Types of dislocations having Burgers vector $a/2$ $[110]$ in the zinc blende lattice (Hornstra 1958).

No.	Symbol of axis	Angle between axis and Burgers vector	Glide plane	Number of broken bonds per cm
1.	$\langle 110 \rangle$	0°	—	0
2.	$\langle 110 \rangle$	60°	$\{111\}$	1.41
3.	$\langle 110 \rangle$	90°	$\{100\}$	2.83 or 0
4.	$\langle 211 \rangle$	30°	$\{111\}$	0.82
5.	$\langle 211 \rangle$	90°	$\{111\}$	1.63
6.	$\langle 211 \rangle$	$73^\circ 13'$	$\{311\}$	2.45 or 0.28
7.	$\langle 211 \rangle$	$54^\circ 44'$	$\{110\}$	1.63 or 0
8.	$\langle 100 \rangle$	90°	$\{110\}$	2.0 or 0
9.	$\langle 100 \rangle$	45°	$\{110\}$	2.0 or 0

One important aspect to recognize in the geometry of the 60° dislocations in GaAs is that the extra half plane can terminate either between the $A\alpha$ planes or between the αB planes. In the former case dislocation ends with a row of say, Ga atoms, while in the latter it ends with a row of As atoms. These two types of 60° dislocations are referred in literature (Hirth and Lothe 1968) as the shuffle set (figure 7) and glide set (figure 8) respectively. A Ga dislocation in the shuffle set corresponds to an As dislocation in the glide set and *vice versa*. This is an important difference to bear in mind when the electrical properties of dislocations are discussed.

One easy way of characterizing dislocations in GaAs is to analyze the microstructure of deformed crystals where dislocations are deliberately introduced. Table 5 shows the types of dislocations observed in the microstructure of Si-doped *n*-type ($n \sim 1.8 \times 10^{18} \text{ cm}^{-3}$) GaAs that has been previously deformed in compression at 550°C to a 3% strain (Swaminathan 1975). The microstructure analysis was performed in the transmission electron microscope where the Burgers vectors are

Figure 8. 60° dislocation of the glide set in GaAs. The extra double plane is indicated by dashed lines. The dangling bonds are left dangling (Blanc 1975).

Table 5. Types of dislocations observed in GaAs deformed in compression at 550°C to strain varying from 3 to 20% (Swaminathan 1975).

Slip plane	Line direction $\vec{l}$	Angle between $\vec{b}, \vec{l}$	Number seen
$\bar{1}11$	$[01\bar{1}]$	60°	7
$\bar{1}11$	$[\bar{1}2\bar{1}]$	90°	6
(010)	$[\bar{1}01]$	90°	2
$\bar{1}31$	$[11\bar{2}]$	73°	2

determined by the standard methods of diffraction contrast analysis (Hirsch *et al* 1965). The Burgers vectors of all the dislocations determined by this method are of the type $a/2 \langle 110 \rangle$. Most of the dislocations are the 60° type though in some cases other types of dislocations are also observed. The dislocations are found to have $\{111\}$ plane which is the primary slip plane (Swaminathan 1975) in GaAs as well as $\{113\}$ and $\{100\}$. The dislocations on the $\{113\}$ planes may probably be grown-in dislocations. In some cases a Lomer dislocation with the slip plane $\{100\}$ is also seen. This is probably the result of the reaction of two glissile dislocations on different $\{111\}$ planes described by the equation

where the two dislocations on the left hand side of the equation glide in $(11\bar{1})$ and $(1\bar{1}1)$ planes respectively. The produced Lomer dislocation lies in (001) plane.

A characteristic feature of the microstructure of deformed GaAs is the presence of long straight dislocations aligned along $\langle 110 \rangle$ and $\langle 112 \rangle$ directions as shown in figure 9. The alignment of dislocations along $\langle 110 \rangle$ and $\langle 112 \rangle$ has been found in other semiconductors as well and it cannot be ascribed to elastic anisotropy. Table 6 shows that covalent materials are no less isotropic than fcc metals in which the phenomenon does not occur. Further it is not obvious that the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions will be low core energy directions. The alignment is presumably due to the low Peierls energy along these directions. The alignment of dislocations along the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions disappears, however, with increasing percentage of deformation as shown in figure 10 where the microstructure resembles that of fcc metals.

Though the primary slip plane in GaAs is the $\{111\}$ plane one can distinguish two types of $\{111\}$ planes in the zinc blende structure. These are the $A\alpha$ and αB planes in figure 6. Since glide in the widely-spaced $A\alpha$ planes involves breaking of the smallest number of bonds, they were suggested to be the slip planes (Shockley

Table 6. Elastic isotropy of fcc metals and of diamond and of zinc blende structure semiconductors. The criterion for elastic isotropy is $C_{11} - C_{12} = 2C_{44}$.

Material	$\frac{C_{11} - C_{12}}{2C_{44}}$
Al	0.82
Ag	0.33
Au	0.35
Cu	0.30
Diamond	0.83
Ge	0.76
Si	0.57
GaAs	0.55
GaSb	0.56
InSb	0.50
ZnS	0.43

Figure 9. Dislocation substructure of Si-doped GaAs deformed at 550° C in compression to a 3% strain (Swaminathan 1975).

Figure 10. Dislocation substructures of Si-doped GaAs deformed at 550°C in compression to a 20% strain (Swaminathan 1975).

1953). However, in the case of αB planes, since glide takes place between closely spaced planes dissociation into partial dislocations can readily occur, which is not the case for dislocations in $A\alpha$ planes as we shall see below.

3.2 Partial dislocation and stacking faults

A stacking fault occurs in the zinc blende structure in the same way as it does in fcc lattices. If the $A\alpha B\beta C\gamma$ stacking sequence of $\{111\}$ planes shown in figure 6c is written as simply $ABCABC$ then the insertion of a B plane results in $ABC B ABC$... i.e., an extrinsic stacking fault and the removal of a B plane results in $A C ABC$ i.e., an intrinsic fault. Because of the stacking of planes in pairs, a low energy fault is formed only between the αB planes (glide set) (Hirth and Lothe 1968). Where a stacking fault ends, a partial dislocation occurs. The partials associated with a 60° dislocation are the analogues of the Shockley partials in fcc lattice; i.e.,

they have Burgers vectors $a/6 [211]$ and $a/6 [\bar{1}21]$.

With the development of weak beam diffraction contrast analysis in the transmission electron microscope (Cockayne *et al* 1969) it has now been established that the dislocations in III-V compounds (Gottschalk *et al* 1978) are dissociated into Shockley partials. In GaAs (Gomez and Hirsch 1978) both α and β dislocations were found to be dissociated and to have the same separation. Even in alloy semiconductors such as Ga(As,P) the dissociation was observed (Mader and Blakeslee 1974). [From the separation of the partials the intrinsic stacking fault energy in undoped n -type GaAs ($n \sim 2 \times 10^{16} \text{ cm}^{-3}$) was estimated to be $48 \pm 6 \text{ erg cm}^{-2}$ (Hirsch 1979a). The stacking fault energy was found to be lower in Te-doped ($n \sim 10^{18} \text{ cm}^{-3}$) and Sn-doped ($n \sim 10^{16} - 10^{17} \text{ cm}^{-3}$) GaAs (Astakhov *et al* 1980) indicating the influence of impurities on the dissociation of dislocations. The observation that dislocations in GaAs as well as in other semiconductors are dissociated raises doubt about the so far accepted concept that dislocations glide in the $A\alpha$ planes (shuffle set) since dissociation in these planes produces a high energy fault. The conflict between mobility and dissociation may be reconciled by a model proposed by Hornstra (1958) for the dislocation in the shuffle set. The idea is that the mobile shuffle set dislocation might associate itself on coming to rest with a pair of partials of opposite sign on the neighbouring glide set planes. The corresponding reaction is

$$\frac{a}{2}[\bar{1}10] + \frac{a}{6}[\bar{1}21] + \frac{a}{6}[\bar{1}21] = a/6[\bar{2}\bar{1}\bar{1}]$$

$$+ \frac{a}{6}[\bar{1}21]$$

Hirth and Lothe (1968) proposed that a dislocation in the glide set can transform to one in the shuffle set and *vice versa* by acquiring a row of either interstitials or vacancies; that is, the process occurs by climb. The energetics of the vacancy and interstitial type shuffle set dislocations in the diamond lattice has been studied by Blanc (1975). The motion of the partial dislocations created in this manner involves shuffling of the bonds and hence is the name shuffle set.

It has been, however, not possible to decide between the glide and shuffle sets by means of electron microscopy since the strain field of the partial dislocations created in the above manner and by the straight dissociation of the glide set dislocation is practically the same. Recently, Hirsch (1981) reviewed this aspect in detail and suggested that the glide set configuration should be favoured. Further experimental and theoretical work are necessary before this question can be settled unambiguously.

3.3 Electrical properties of dislocations

The early pioneering work of Shockley (1953) and Read (1954) on dislocations in diamond cubic structure showed that a 60° dislocation has a row of atoms each with an unpaired bond (dangling bond) along the edge of the extra half plane. For dislocations in the $\{111\}$ planes the line density (d) of such bonds is equal to $(2/\sqrt{3}b) \sin \theta$ where θ is the angle between the dislocation line and the Burgers vector b . Accordingly, the screw dislocation does not have any dangling bond. The presence of these dangling bonds form the most important feature of dislocations in semiconductors determining to a large extent the electrical and the optical properties of dislocations.

The unsaturated dangling bond along the dislocation in Si or Ge can either accept another electron to satisfy the bond or donate its electron and in this sense the dislocation can act as an acceptor or a donor. Because of the translational symmetry along the dislocation it is supposed to form an one-dimensional band (Shockley 1953), the band width and the mobility in the band being determined by the overlap of wave functions of electrons on neighbouring atoms along the dislocation. In GaAs, because of the different core structure of the α and β dislocations they would be expected to have different electrical characteristics.

The electrical behaviour of dislocations in III-V compounds has been studied in detail only for InSb. Specimens which were bent to introduce a surplus of In- or Sb-dislocations exhibited differences between the two types of dislocations. In *n*-type InSb Gatos *et al* (1961) found that the In-dislocations act as acceptors while Sb dislocations act as donors. Bell *et al* (1966) on the other hand reported acceptor action for both dislocations in *n*-type InSb and donor action for Sb dislocations in *p*-type InSb. In *p*-type InSb Baitinger *et al* (1969) found only an acceptor action for Sb dislocations but both acceptor and donor behaviour for In dislocations. Recently Labusch and Schröter (1980) suggested that a possible reason for these conflicting results could be the difficulty in identifying whether the dislocation in question belongs to the shuffle set or the glide set. This is important because as we noted earlier an In dislocation in the glide set is a Sb-dislocation in the shuffle set and *vice versa*.

Information about the electronic states of dislocations in GaAs are very scarce. The electrical properties of dislocations are generally deduced from measurements made on deformed samples. From Hall measurements on Cr-doped high resistivity GaAs bent at 580°C to produce an excess of α -dislocations, Lin and Bube (1975) observed an increase in the electron concentration after deformation. On the other hand, Esquivel *et al* (1976) observed a decrease in carrier concentration and mobility

in *n*-type Te-doped and undoped GaAs which has been previously bent to introduce an excess of either α or β -dislocations with the decrease being larger in samples containing β dislocations. Similar observations were made by Nakata and Ninomiya (1977) in *n*-type GaAs and by Gwinner and Labusch (1979) in both *n* and *p* type undoped GaAs with a difference namely that the sample with α -dislocations showed a larger decrease in the carrier concentration (Gwinner and Labusch 1979). These results suggest acceptor and donor action for the dislocations in *n*- and *p*-type samples respectively. From analyzing spectral response and decay process of photoconductivity in bent undoped *n*-type GaAs, Nakata and Ninomiya (1979) deduced two dislocation levels, one at 0.7eV and another at 0.9eV below the conduction band edge and they were attributed to two partial dislocations. Deep level transient spectroscopic measurements (Ishida *et al* 1980) on undoped *n*-type GaAs which has been deformed under compression indicated no electron trap but a broad unresolved hole trap spectrum presumably due to overlapping dislocations of different character.

Theoretical calculations by Farvacque and Ferre (1980) predicted deep levels for both α and β dislocations in GaAs. Oberg (1978) using a Slater-Koster approach found that the 60° Ga and As dislocations act as acceptors in *n*-type and the As-dislocations act as donors in *p*-type GaAs. Both these calculations were made for perfect dislocations belonging to the shuffle set. This may be unrealistic in view of the experimental evidence that dislocations in GaAs are dissociated. Further the uncertainty whether a particular dislocation observed in an experiment is the glide type or shuffle type is another problem in comparing experiment and theory.

Finally there are two other points worth mentioning in the discussion on the electrical properties of dislocations. Firstly, the electrical nature of the dislocation is a natural consequence of the presence of unsaturated 'dangling' bonds along the dislocation. This picture holds good even for the screw dislocations in light of the new evidence from EPR measurements on deformed Si which indicates that even they contain dangling bonds (Alexander 1979). It is, however, possible that the dangling bonds at the end of the dislocation interact and get eliminated as a result. For example, the 90° edge dislocation in {100} plane has the two dangling bonds per atom which can undergo reconstruction eliminating dangling bonds (Hornstra 1958). Further, calculations by Marklund (1979) and Jones (1979) on partial dislocations in Si and Ge suggest that reconstruction should be energetically favoured. In fact, such a reconstruction was suggested to be the reason for the absence of carrier recombination at an edge sessile dislocation in (Ga, Al) (As, P) heterostructures (Petroff *et al* 1980). This may also be the reason why no dislocation induced luminescence was observed in deformed GaAs (Bohm and Gwinner 1978).

Secondly, some of the electrical effects in deformed GaAs such as the decrease in the carrier concentration and mobility could very well be due to point defects. For example, at the temperature of deformation, impurities in GaAs could diffuse and precipitate near dislocations and thus the changes in resistivity would merely be a result of this gettering near dislocations. This also emphasizes the need for high purity GaAs samples for the experiment. Another possibility is the creation of a high density of point defects during deformation due to

dragging jogs on screw dislocations as shown for example in Si (Weber and Alexander 1977 and Kimerling and Patel 1979) and Ge (Albers *et al* 1977). Ishida *et al* (1980) found in a DLTS study on deformed GaAs that two electron traps and a hole trap which were present in the as-grown material increased with plastic deformation. These may very well be related to point defects. Since there could be a concentration of these point defects near the dislocation a simple interpretation of the electrical results in deformed GaAs may be incorrect.

3.4 Mechanical properties of GaAs and dislocations

The addition of dopants has a profound influence on the dislocation velocity and thus the mechanical properties of GaAs. Several investigators (Sazhin *et al* 1966, Laister and Jenkins 1973 and Swaminathan and Copley 1975a) have noted that addition of *n*-type dopants like Si, Te increases the yield stress while that of *p*-type dopants like Zn decreases the yield stress. This effect was confirmed in dislocation velocity measurements as well (Choi *et al* 1977). Though there were differences in the effects of doping on the different types of dislocations, in general the velocity of the dislocation was decreased with *n*-type doping and increased with *p*-type doping consistent with the yield stress measurements.

To explain the effect of a small amount of impurity (typically around 10^{18} cm^{-3}) it has been proposed (Sazhin *et al* 1966; see also Kirkby 1975) that dislocations are pinned by impurity atmospheres. Swaminathan and Copley (1975a) argued against the pinning model because of their observation that yielding was gradual and not abrupt, the latter phenomenon being characteristic of dislocation pinning. In view of the small concentration of impurities, Swaminathan and Copley (1975a) proposed that hardening in *n*-type GaAs occurs by the interaction of mobile dislocations with asymmetrical defects such as donor-vacancy impurity complexes. Swaminathan and Copley (1975b) investigated in detail the effect of various thermal and thermomechanical treatments on the yield stress of heavily Si-doped GaAs and developed a point-defect model to explain the observed behaviour in terms of changes in the concentration of ($\text{Si}_{\text{Ga}} - \text{V}_{\text{Ga}}$) pairs.

Alternate theories have been proposed especially in Si and Ge to explain the effects of doping on dislocation velocity (Haasen 1975; Patel *et al* 1976; Schröter *et al* 1977; Patel and Testardi 1977) based on the influence of doping on the line charge of the dislocation and thus on the formation and/or motion of double kinks on the dislocation. Recently Hirsch (1979b) proposed another model where he assumed localized electronic states associated with kinks and the doping effect was considered to be due to the change in the charge states of the kinks themselves. Though such electronic effects may be important in doped GaAs as well especially at low deformation temperatures, a comprehensive theory taking into account the elastic/electronic interaction between dislocations and asymmetrical impurity complexes is needed to understand the dislocation motion. Such a study is also important from a practical point of view in that a major failure mechanism of GaAs-(Al, Ga)As heterostructure lasers has been attributed to the motion of dislocation networks known as dark line defects (§ 4).

3.5 Control of dislocation density in GaAs

Since dislocations generally cause deleterious effects in devices (§ 4), it is aimed to grow dislocation free material as far as possible. Dislocations in the growing crystal can be introduced in a variety of ways:

- (i) Thermal stresses causing plastic deformation.
- (ii) Condensation of the excessive point defects present near the growth temperature to form prismatic dislocation loops.
- (iii) Defective seed crystal or accidental introduction of macroscopic foreign particles during growth causing generation and multiplication of dislocations.

Of these three, the first two are the most important aspects to be considered. Brice and King (1966) and Brice (1970) noted that the partial pressure of As during growth is a parameter for controlling the dislocation density in horizontal Bridgman crystals and pulled crystals. A low partial pressure of As was recommended so as to reduce the concentration of V_{Ga} and thus the concentration of prismatic loops.

Perhaps the principal mechanism by which dislocations are incorporated in the crystal is the plastic deformation caused by excessive thermal stress (Osvenskii and Eremeev 1971 ; see also Jordan *et al* 1980 and references therein). A detailed analysis of this problem in GaAs is to be found in the paper by Jordan *et al* (1980). They concluded that dislocations in pulled crystals cannot totally be avoided unless $h \gtrsim 0.02 \text{ cm}^{-1}$ for $\Delta T \sim 200^\circ\text{C}$ where h is the heat transfer coefficient and ΔT is the temperature difference between the melting point of GaAs and the ambient temperature. In this regard these authors suggested the incorporation of radiation shields and an after-heater in the growth system.

Since the dislocation generation in the as-grown crystals is caused by plastic deformation, dopants which increase the yield stress would tend to lower the dislocation density. We noted in § 3.4 that the yield stress increases by the addition of donors and decreases with acceptors. Addition of donor impurities giving carriers $1 - 8 \times 10^{18} \text{ cm}^{-3}$ led to a substantial reduction in the dislocation density while addition of acceptor impurities even up to the solubility did not have any effect (Osvenskii and Eremeev 1971 and Belyatskaya *et al* 1972). The addition of donors also resulted in a significant rearrangement of the dislocations. This is presumably because of the high vacancy concentration in doped crystals facilitating dislocation climb. In fact Swaminathan and Copley (1975b) found that the microstructure of Si-doped GaAs sample which has previously been annealed to produce a high density of prismatic dislocation loops was found to be free from loops and glide dislocations after deformation to a few per cent strain and recovery at 400°C for a few hours.

4. Effects of native point defects and dislocations on devices

It is now generally accepted that native defects and dislocations have profound influences in determining the quality and performance of semiconductor devices.

However, the correlation between device characteristics and defects has remained qualitative. The reason for this is that it is often difficult to isolate pure dislocation effects when possibility of dislocation-point defect interaction exists. In the case of native defects it has been even more difficult to correlate device parameters with any specific native defect. The implication of such defects is often based on circumstantial evidence. For example, the thermally damaged layer present on semi-insulating GaAs substrates during the growth of epitaxial films has been found to have adverse effects on the performance of microwave FET devices (Barrera 1975). The problem has been ascribed to V_{As} or impurity- V_{As} complexes (Lum *et al* 1977). This is a natural assignment since during baking of the substrates in an open system at high temperatures prior to epitaxial growth, As escapes from the crystal giving rise to V_{As} . The V_{As} related defects have been thought to be the cause of the p -layer formation on the substrates. Recently, Klein *et al* (1980) showed that Mn present in the Cr-doped substrates diffused to the surface during heat treatment. Since Mn is an acceptor in GaAs, the type conversion could very well have been caused by it.

Ettenberg (1976) found in vapour grown GaAs that both the minority carrier diffusion length and life time decrease with increasing As/Ga ratio during growth. Since the formation of V_{Ga} is favoured with increasing As/Ga ratio, the observed effects are attributed to it. A similar implication was made by Kasano (1978b) for degradation of vapour grown GaAs. Again both these effects could have been caused by some impurity or some other Ga deficient nonstoichiometric defect.

There is perhaps less ambiguity about the effects of dislocations. (For some earlier references see the review by Petroff 1975). Dislocations reduce the minority carrier diffusion length and when it is comparable to the spacing between them the luminescence efficiency decreases (Ettenberg 1974). High resolution

Figure 11. Typical isointensity luminescence map in the vicinity of a dislocation in GaAs. The numbers indicate the intensity in arbitrary units for the near gap luminescence at 1.513 eV at helium temperatures (Heinke and Queisser 1974).

Figure 12 A, B. see page 432 for caption

Figure 12 (C)

Figure 12. (A) EBIC micrograph of misfit dislocation network. (B) Monochromatic ($\lambda=790\text{ nm}$) CL micrograph of the same area. The non-radiative recombination centres appear as dark areas. (C) The STEM micrographs correspond to the framed area shown in (A) and (B). The operating Bragg reflections are (220) and $(\bar{2}20)$ and the incident electron beam is parallel to $[001]$ (Petroff *et al* 1980)

photoluminescence scanning around dislocations at low temperatures (Heinke and Queisser 1974) showed that the intensity of band edge emission decreases near a dislocation within a cylinder of $20\text{ }\mu\text{m}$ radius around it (figure 11). The authors also noted that the effect is greater near freshly introduced dislocations than grown-in dislocations by nearly three orders of magnitude. A similar observation was also made earlier by Osvenskii *et al* (1971). However, Böhm and Fischer (1979) disputed this result and noted that both grown-in and deformation induced dislocations behave similarly. Further they made a significant observation that the larger effect of deformation induced dislocations as noted by Heinke and Queisser (1974) was indeed due to Cu segregating near dislocations. The importance of such impurity-dislocation interaction was also evidenced in the results of Vovnenko *et al* (1979) who reported an increase in the internal quantum efficiency of some deep centre luminescence in deformed GaAs. Though such effects could mask dislocation effects it is generally true that dislocations act as nonradiative centres. This is clearly shown in figure 12 for dislocations in $\text{Ga}_{1-x}\text{Al}_x\text{As}_{1-y}\text{P}_y$ heterostructures grown by LPE. Dislocations labelled D_2 , D_3 and D_4 act as nonradiative centres giving dark contrast. Dislocation D_1 which does not exhibit any contrast has been assigned to a neutral edge dislocation.

That dislocations act as nonradiative centres is further shown by Roedel *et al* (1979) who investigated the effect of dislocations in graded bandgap Si-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ light emitting diodes. This is shown in figure 13. The external quantum efficiency of the diodes is found to decrease with increasing dislocation density in the LPE wafers.

Dislocations are also known to be the cause of the rapid degradation of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ -GaAs injection lasers and LEDs. The degradation has been linked to linear defects known as dark line defects (DLDs). The DLDs have been

Figure 13. A plot of the efficiency *vs* dislocation density for 45 individual LEDs and the results of the substrate mapping experiment and the theoretical approximation for $\eta(\rho)$ dashed line (Roedel *et al* 1979).

Figure 14. Plot of the time to failure (filled symbols) or the accumulated testing time (open symbols) for lasers operated at 3 mW at 70°C vs the cumulative percent of devices with times less than or equal to that time, on a normal scale. The Ga (As, Sb) devices have GaSb concentrations of between 0.4 and 2 mole % while the GaAs controls have GaSb concentrations of zero or less than 0.1 mole %. These were grown on substrates which had dislocation densities of $< 3 \times 10^3 \text{ cm}^{-2}$. The (GaAs) Sb lasers grown on defective substrates had substrates with dislocation densities of $\sim 4 \times 10^4 \text{ cm}^{-2}$. Not all devices were monitored at fraction of hour intervals for times less than one hour (Anthony *et al* 1981).

identified by transmission electron microscopy as three dimensional dislocation networks consisting of long dislocation dipoles and small dislocation loops. The DLDs originate from a precursors defect known as dark spot defects (DSDs) which themselves nucleate from threading dislocations in the device active layer. Figure 14 compares the lifetime at 70°C of two classes of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ injection lasers having Ga(As, Sb) active layers. The devices which have poor 70°C median lifetimes were made from LPE wafers which were grown on substrates having a dislocation density of $\sim 4 \times 10^4 \text{ cm}^{-2}$ as compared to the good devices for which the substrates had dislocation densities $< 3 \times 10^3 \text{ cm}^{-2}$ (Anthony *et al* 1982). The probability of a dislocation threading through the active layer and hence that of DLD formation increase with increasing number of dislocations in the substrates and thereby affecting the laser operating lifetime.

The growth of the DLDs which may nucleate at the threading dislocations occurs very rapidly (10^{-6} – 10^{-2} cm/sec) (Petroff and Hartman 1974; Monemar and Woolhouse 1976) and the growth rate is dependent on the injection current of the laser. The DLDs propagate usually in $\langle 100 \rangle$ direction and occasionally in

$\langle 110 \rangle$ direction. While the DLD in the $\langle 110 \rangle$ direction has been shown to be caused by carrier injection enhanced (Kimerling and Lang 1975) dislocation glide (Kamejima *et al* 1977) there is controversy about the $\langle 100 \rangle$ DLD. A pure climb process involving either the absorption of interstitials or the emission of vacancies has been invoked to explain the observed $\langle 100 \rangle$ DLD structure (Petroff and Hartman 1974 and Hutchinson and Dobson 1975b). On the other hand, Matsui *et al* (1975) proposed a glide mechanism for the initial stage of the DLD growth in the $\langle 100 \rangle$ direction and a combination of glide and climb for the final development of the observed structure. The important point that emerges from these models is that climb plays an important role in DLD growth. There is, however, considerable uncertainty about the nature and origin of the point defects required for climb. We will refer the reader to the book on heterostructure lasers by Casey and Panish (1978) for a discussion of these topics. We will discuss only a few recent works here.

Hutchinson *et al* (1978) investigated the dislocation structures in annealed Te-doped GaAs after optical pumping. The annealing treatment was such that it produced in the samples prismatic dislocation loops which were assigned to interstitials based on transmission electron microscopic contrast analysis. A $1\text{ }\mu\text{m}$ layer of $\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ was grown by LPE on the annealed GaAs sample which was then optically pumped with a 7510Å line of a Kr laser at the power density of $5.7\text{--}7.9 \times 10^4\text{ W/cm}^2$ for times varying from 1 to 80 min. The pumped regions were investigated by transmission electron microscope. Hutchinson *et al* observed that optical pumping caused the loops to undergo considerable climb and develop into long dislocation dipoles. The extent of the climb was found to increase with pump power and time. Since the presence of the prismatic interstitial dislocation loops in the sample which has been equilibrated prior to optical pumping implied that the concentration of free interstitials in solution is very small, it was concluded that climb had occurred by vacancy emission from the dislocation. The latter process was supposed to have been caused by the energy released in the recombination process (O'Hara *et al* 1977). Hutchinson *et al* 1978 proposed that the vacancies emitted in this process are not observable by transmission electron microscope as they might aggregate to form submicroscopic clusters. The major difficulty in accepting this model unequivocally is the controversy regarding interstitial vs. vacancy dislocation prismatic loop in annealed GaAs (see § 2.4)

Wakefield (1979) examined the effect of strain on the photoluminescence degradation in oxide striped (Ga,Al) As double heterostructure lasers and found that dark bands were observed in regions where the dilation was a maximum. The photoluminescence degradation was attributed to recombination enhanced migration of point defects to the strained region. Since regions of tension were degraded, the point defects were suggested to be interstitial atoms. This conclusion is in agreement with the viewpoint that DLD climb occurs by the absorption of (and concomitant emission of) interstitials (vacancies).

Using a scanning deep level transient spectroscopy technique Lang *et al* (1979b) investigated the interaction between dislocation climb networks and the so-called DX centres (see § 2.4) in (Ga, Al) As heterostructures. These authors found that near the dislocation climb network the concentration of the DX centres decreased by $\sim 40\%$ (figure 15). This suggested that there is an interaction

Figure 15. Steady-state current (EBIC) and transient-detrapping-current (SDLTS) intensities as a function of the beam position for a beam scanning across a $\langle 100 \rangle$ dark line (DLD). The specimen temperature is $T = -26^\circ\text{C}$ to display the DX-centre distribution with the SDLTS line scan (Lang *et al* 1979).

between the DX centres and the dislocation network. It is not, however, clear whether the DX centres are themselves the source of the point defects involved in the climb process because of the apparent conflict between the proposed vacancy nature of the DX centre (Lang *et al* 1979a) and interstitial nature of the dislocation network. To resolve this contradiction Lang *et al* hypothesized that the change in the DX centre occurred before the climb process and that the decay of the centre during electron-hole recombination might proceed by the emission of Ga_i . Recently, Frank and Gösele (1980) reiterated the earlier model proposed by Petroff and Kimerling (1976) that dislocation climb occurs by absorption of Ga_i and speculated that the DX centres might in fact be Ga_i .

Figielski (1980) made a new proposal to explain the degradation of lasers. He suggested that during carrier injection bond breaking and reconstruction occurs. This process originates at a seed dislocation. During such reconstruction, migration of the broken dangling bond occurs leaving behind a line defect. The line defect thus created may be screw or a helical dislocation. Figielski further suggested that the dislocation dipoles could develop by interstitial pipe diffusion along the helical dislocations. This model according to Figielski explains at least the highly directional nature of dislocation dipoles, the high velocity of dipole propagation, unusual dipole configuration and shape and the role of carrier injection in the process. It may be interesting to check this hypothesis by optically pumping GaAs substrate material which contains helical dislocations introduced by a suitable previous annealing treatment.

Hutchinson and Dobson (1980) reported an asymmetry in the climb rate, that is, the α dislocations (shuffle set) climb much more rapidly than the β dislocations (shuffle set) indicating that the climb process depends on the structure of the dislocation core. This might play an important role in the point defect-dislocation interaction necessary for the climb. Imai *et al* (1979) also suggested that the fast and slow DLDs might be dominated by $\sim \alpha$ and β dislocations respectively.

We will conclude this section with an observation by Petroff (1981) that the nature of the DLD structure in lasers grown by liquid phase epitaxy or molecular beam epitaxy are identical. Petroff suggested that the inhomogeneity in the interfaces of the LPE structures and point defects intrinsic to the MBE structures could be one of the likely sources of point defects for DLD growth. Petroff further noted that dislocations in multiquantum well superlattices are not nonradiative centres. This finding suggests the possibility of making more reliable lasers with such structures.

5. Conclusions

We have given a comprehensive review of defects in GaAs with emphasis on native point defects and dislocations. The current state of knowledge on point defects does not allow us to draw a unified defect model for several reasons. First, the question of the dominant native defects in equilibrium is unsettled. This is important both from a fundamental and technological point of view. Hurle (1979) proposed the Frenkel disorder in the As-sublattice as the dominant disorder in equilibrium. Recent EPR result of Wagner *et al* (1980) suggests the presence of As_{Ga} defect. Further the acceptors observed after heat treatment at low As pressure could be assigned to Ga_{As} instead of V_{As} as had been done. The As_{Ga} defects could perhaps also be invoked to explain the lattice parameter and density increases at high As pressure. These considerations imply that the antistructure disorder should be considered in the future point defect models. Second, the conflict regarding the nature of the prismatic dislocation loop observed by transmission electron microscope in annealed GaAs doped with donor impurities remains. Is the prismatic loop interstitial like or vacancy like? If both are possible under what conditions the formation of one type is favoured over the other?

The nature and origin of point defects involved in the climb of dark-line defects during degradation of GaAs lasers are still unknown. The climb process in GaAs requires point defect in equal supersaturation in both sublattice. Since this is rather unlikely, Petroff and Kimerling (1976) proposed a new model in which supersaturation of only one point defect is needed for the dislocation climb. While they proposed climb by the absorption of interstitials O'Hara *et al* (1977) and Hutchinson *et al* (1978) suggested that climb occurs by the emission of vacancies. Further, the role of anti-site defects, dissociations of dislocations and the different types of dislocations are factors still not considered in the climb process.

There is at present no satisfactory way of distinguishing between the shuffle set and the glide set dislocations in a particular experiment. This introduces a difficulty in deducing the electrical nature of the dislocations. Further since the core structure of the α and β dislocations are different and that the α dislocation in the shuffle set corresponds to the β dislocation in the glide set, point defect-dislocation interaction effects would be different for the two sets. Recent high resolution electron microscopy experiments by Olsen and Spence (1981) to distinguish the glide and shuffle sets are encouraging in this respect.

Finally, annealing experiments on high purity GaAs samples as a function of As pressure are needed to find whether donors or acceptors are created at the low As side. Care must be taken to prevent Cu contamination in these annealing experiments. It is also necessary to combine two or more techniques to analyse the same sample. In this respect, new experimental techniques may have to be employed. The recent success with EPR experiments (Wagner *et al* 1980) raises the hope for more direct evidence for point defects. To a limited extent positron lifetime measurements have also been used (Gopinathan *et al* 1977; Cheng *et al* 1979) and they implicate V_{Ga} related defects. Positron lifetime together with 2γ angular correlation measurements would be helpful. Recently, Mössbauer spectroscopy has also been used to study Sn implanted GaAs (Holm and Weyer 1980) giving evidence for Sn-vacancy complexes. Ballistic phonon attenuation measurements in $Ga_{1-x}Al_xAs$ (Narayanamurti *et al* 1979) substantiated the impurity - V_{As} model for the DX centres. The potential of internal friction measurements has not yet been fully utilized in GaAs. Perhaps in the future these measurements would be expected to be employed to understand and control the defect structure of GaAs.

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