JOURNAL OF MATERIALS SCIENCE 6 (1971) 1389–1396

A Study of non-stoichiometry in Gallium Arsenide by Precision Lattice Parameter Measurements

A. F. W. WILLOUGHBY, C. M. H. DRISCOLL
Engineering Materials Laboratories, The University, Southampton, UK

B. A. BELLAMY
Solid State Division, Atomic Energy Research Establishment, Harwell, UK

An automatic method of precision lattice parameter measurement, capable of repeated measurement at intervals across single crystals with an accuracy of better than one part in 10^6, has been applied to gallium arsenide. The technique has been used to compare homogeneity of material grown from the melt with that prepared by vapour and liquid epitaxy, to study material grown from the melt under various pressures of arsenic, and to investigate the effect of heavy doping on the lattice parameter. The technique is shown to provide new and interesting information on defects in gallium arsenide.

1. Introduction

The possibility that gallium arsenide exhibits a significant degree of non-stoichiometry is of great interest in view of the important applications of this semiconducting compound. This possibility was first suggested by Straumanis and Kim [1] who noted that the lattice constant, obtained on powdered samples by X-ray diffraction, of material heated with gallium at 1000°C for 18 h was 5.65326Å (at 25°C), whereas that of material heated with excess arsenic at the same temperature and time was 5.65298Å, while material believed to be stoichiometric had a lattice parameter of 5.65321Å. With concurrent density results Straumanis and Kim deduced that the phase width extended from 49.998 to 50.009% arsenic, which implies the presence of non-stoichiometric defects at a concentration of order 10^{19} cm^{-3} in the arsenic-rich material; a number far in excess of the usual impurity content in gallium arsenide; the density results on material prepared under different conditions of non-stoichiometry, however, were not significantly different, and this must cast doubt on their conclusions as to the type and concentration of defects. The presence of a large number of defects ($\sim 10^{19}$ cm^{-3}) in gallium arsenide has been indicated indirectly by internal friction [2], paramagnetic resonance [3] and electrical [4] measurements, while the arsenic pressure dependence of the diffusion rate of zinc [5] and manganese [6], the identification of photoluminescence centres [7, 8] which are found only under non-stoichiometric conditions, the thermal conversion of *n*-type samples after annealing under excess arsenic conditions [9-11] provide strong evidence for the existence of non-stoichiometry in the solid. Potts and Pearson [12] have observed large increases ($\Delta a/a$ of the order 10^{-3} to 10^{-4}) in the room temperature lattice parameter, measured by the Kossel line technique, of gallium arsenide single crystals heated under the equilibrium arsenic partial pressure, and subsequently quenched from temperatures above 1000°C; the effect being greatest in samples quenched closest to the melting point, and being considerably depressed after heating in an arsenic overpressure with subsequent quenching. Subsequent heat treatments at room temperature and high temperatures after quenching, showed large decreases in lattice parameter with time, which appeared to proceed in two stages; the first rapid annealing stage was associated with recombination of arsenic vacancies and

© 1971 Chapman and Hall Ltd.

arsenic interstitials, and the second slower stage with arsenic vacancy diffusion, the arsenic overpressure effect being interpreted in terms of As monovacancies. It must be pointed out, however, that the arsenic overpressure effect refers to one sample only , and that the residual strain found to be present after annealing quenched samples emphasises the uncertain role of quenching strains in such experiments.

Recent techniques [13, 14] allow the precision measurement of lattice parameter on single crystals on which electrical measurements can also be made, which was not possible in the case of powdered samples. The fully automated nature of this technique [14] also allows quick and convenient measurements of lattice parameter at intervals across each sample, and its uniformity can thus be measured. Pierron and McNeely [15] recently found variations in lattice parameter of a few parts in 10^5 across melt grown and solution grown gallium arsenide samples, but samples grown by vapour epitaxy were uniform to within about five parts in 10^6.

The objects of the present investigation were thus a more rigorous study of the uniformity of gallium arsenide crystals grown by various techniques, and an investigation, for the first time on single crystal material, of the degree of non-stoichiometry of the compound. The results of the uniformity studies are presented in section 3.1 and those of the non-stoichiometry studies in 3.2. The results are discussed in relation to previous work and to the expected nature of non-stoichiometric defects in this material.

2. Experimental

2.1. Sample Preparation

Gallium arsenide crystals grown by a variety of techniques have been examined in this investigation. Samples grown from the melt by liquid encapsulation pulling have been supplied by RRE, Malvern, and crystals grown from the melt by the horizontal Bridgman technique have been supplied by the Allen Clark Research Centre (Plessey Co) and Mullard Laboratories (Redhill). The latter series of samples were grown with a different arsenic reservoir temperature (from 609 to 637°C) for each sample; the acceptable range of temperatures in the melt furnace was found to be between 1240 and 1260°C. Gallium arsenide layers grown by liquid epitaxy (i.e. from gallium-rich solution) have been supplied by Mullard Laboratories and SERL (Baldock), the latter being heavily doped n-type layers. Layers grown by vapour epitaxy have been supplied by the Allen Clark Research Centre (Plessey Co). The growth temperatures of the various epitaxial material used in this investigation are shown in table I.

The melt-grown samples were sectioned for lattice parameter measurement parallel to a $\{100\}$ plane (within 2°) by means of a diamond saw. The cut specimens were then ground with 600 grade silicon carbide powder and chemically polished with a solution of three parts nitric acid, one part hydrofluoric acid and one part water. In view of the large effect of surface damage on the lattice parameter observed by Pierron and McNeely [15], although their conclusions are of dubious value without line profiles, care was taken to ensure that all surface damage had been removed by measuring the lattice parameter after successive chemical polishes. Since no significant change in the lattice parameter was detected after repolishing it was concluded that the removal of surface damage was complete. The layers grown from gallium-rich solution were grown on $\{100\}$ substrates and free gallium was removed before mounting. The prepared sample was mounted on the X-ray goniometer using silicone grease to obtain a strain-free mounting [14].

2.2. Lattice Parameter Measurement

The technique used was based on that described by Bond [13] in which eccentricity, absorption and zero errors are eliminated by measuring the angle between two reflecting positions of the crystal rather than the position of the reflected beam. The automatic precision X-ray goniometer [14], used in this investigation, renders this technique capable of an accuracy of one part in 10^7 and allows repeated lattice parameter measurements to be made automatically at intervals across samples. The setting up, specimen adjustment, measurement and calculation procedure have been described in a previous publication [14] which gives full details of the method. The reflection used for this investigation was (800) (with Cu $K\beta$ radiation; $\lambda = 1.39217$ Å) at a Bragg angle of about 80°. All the samples were kept at a temperature of 27.2 ± 0.1°C by means of a temperature controlled enclosure; and were scanned at 1 mm intervals with a beam width of 1 mm at the specimen surface. Thus, there was no overlap between neighbouring regions of the crystal scanned by the X-ray beam. A typical line profile is shown in fig. 1.

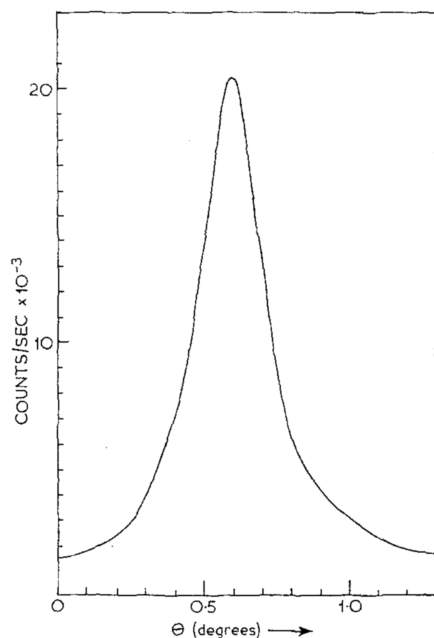

Figure 1 Typical line profile obtained in this work (800 reflection, CuKβ radiation).

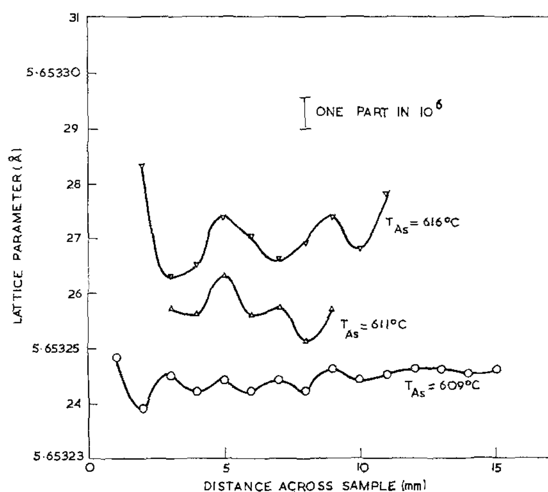

Figure 2 Lattice parameter scans across three samples grown by the horizontal Bridgman technique, for various arsenic reservoir temperatures (T_{As}).

3. Results

3.1. Lattice Parameter "Scans"

3.1.1. Melt-grown material

Typical lattice parameter scans across horizontally-grown samples are shown in fig. 2. The variation across each sample was less than three parts in 10^6, as shown in the figure, and each curve could be reproduced closely by repeated backward and forward scanning. This repeated scanning confirmed that the reproducibility of each measurement, which was limited in these experiments by the counting statistics, was better than one part in 10^6. Fig 2 also includes. the arsenic reservoir temperature during the growth of each sample; and suggests a systematic increase of lattice parameter with arsenic pressure. This indication of non-stoichiometry will be discussed in more detail in section 3.2. The lattice parameter scans in fig. 2 are typical of horizontally grown samples. The uniformity of lattice parameter was not strongly dependent on the scanning direction, but scans parallel to the growth direction generally showed less variation than in other directions. Material grown by liquid encapsulation pulling was generally less uniform than the horizontally grown material, and variations of lattice parameter across these samples were of the order of one part in 10^5. However, the lattice parameters at 27.2°C of all the melt-grown samples examined in this study (thirteen crystals in all), with the exception of one sample M1 grown by liquid encapsulation pulling, differed by no more than about one part in 10^5, and these measurements all lie within the shaded band in fig. 3, i.e. between 5.65324 and 5.65330Å. The low value of sample M1 is, as yet, unexplained.

3.1.2. Solution-grown samples

Measurements on four undoped liquid epitaxial layers grown by Mullard Laboratories (Redhill) gave mean lattice parameter values within the range 5.65324 to 5.65330Å, i.e. similar to the range exhibited by melt-grown samples. In fig. 3 a scan on a typical liquid epitaxial film LE3 (thickness = 73 μm) is shown and this lies within the shaded band representing the limits of values obtained on melt-grown samples. Scans of other undoped liquid epitaxial samples were approximately as uniform as LE3 and varied by about one part in 10^5 across each sample as shown in table I. The mean lattice parameter values of LE2, 3 and 4 showed a slight increase with increasing gallium content in the liquid at the beginning of growth (see table I) although the effect is not clearly defined owing to a relatively large degree of non-uniformity across each sample and the overlapping growth temperature ranges.

Heavily doped layers grown by liquid epitaxy,

TABLE I The growth temperature and mean lattice parameter of epitaxial GaAs

Sample identification*	Sample thickness (microns)	Substrate temperature °C	Mean lattice parameter, with the standard deviation from the mean, at 27.2 ± 0.1 °C
LE1	40	cooled from 881.2 to 808.7	5.653250 ± 0.000005
LE2	125	828.8 to 812.7	5.653245 ± 0.000013
LE3	73	812.7 to 791.8	5.653251 ± 0.000003
LE4	50	781.2 to 766.5	5.653253 ± 0.000013
LE5 (Te-doped)	100	from 950°C down	5.654323 ± 0.000022
LE6 (Sn-doped)	20	at 600°C	5.654201 ± 0.000046
VE1	144	—	5.653276 ± 0.000030

*The prefix LE refers to gallium arsenide layers grown by liquid epitaxy, while the prefix VE refers to those grown by vapour epitaxy.

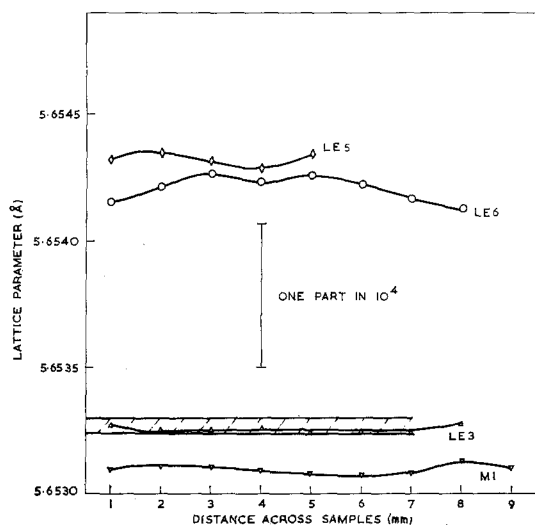

Figure 3 Lattice parameter scans on liquid epitaxial layers LE5, LE6 and LE3, and a melt-grown sample M1. All measurements on melt-grown samples (except M1) lay within the shaded band shown. LE3 is undoped, LE5 and LE6 are doped with 1×10^{19} cm^{-3} of Te and 1×10^{19} cm^{-3} of Sn respectively.

which were supplied by SERL (Baldock) have also been examined in this way. Fig. 3 shows scans across two samples LE5 and LE6, doped with 1×10^{19} cm^{-3} of Te and 1×10^{19} cm^{-3} of Sn respectively (thickness 100 μm and 23 μm respectively). The lattice parameters of both of these layers are at least one part in 10^4 higher than those of undoped layers, as shown in the figure. Such an increase is reasonable since the radius of both the Sn and Te atoms, ionic or covalent, is larger than the radius of either the Ga or As atom in GaAs. The effect of doping additions on the lattice parameter is discussed more generally in section 4.3.

3.1.3. Vapour epitaxy sample

Measurements on a vapour epitaxy sample grown at the Allen Clark Research Centre (Plessey Co) gave a mean lattice parameter value within the range 5.65324 to 5.65330Å; this sample did not appear to be as uniform as the undoped solution-grown epitaxy samples.

3.2. The Effect of Arsenic Pressure on Lattice Parameter

The systematic increase of lattice parameter with arsenic pressure suggested by the results presented in fig. 2 was investigated more extensively on horizontally grown samples prepared at arsenic reservoir temperatures from 609 to 637°C. Fig. 4 is a plot of the average lattice parameters of this series of samples against the arsenic content in the melt, calculated from the arsenic reservoir temperature (also shown in the figure) using the data of Honig [16] to obtain arsenic pressures and that of Boomgaard and Schol [17] to obtain melt concentrations. Each measurement in fig. 4 was made at 27.2° ± 0.1°C over the same part of the main gear wheel to minimise relative errors; the spread indicated by the bar on each point represents the non-uniformity of each sample and is the standard deviation of all the measurements in the scan across that sample (these bars do not represent the reproducibility at any point on a sample, which was in all cases better than one part in 10^6). It is evident from fig. 4, despite scatter, that increase in arsenic reservoir temperature from 609 to 637°C produces an increase in lattice parameter of about six parts in 10^6. This trend, shown in fig. 4, has been confirmed in repeat series of measurements, an example of which is shown in fig. 5. The lattice parameter values differ from those in fig. 4 because in each case relative and not absolute

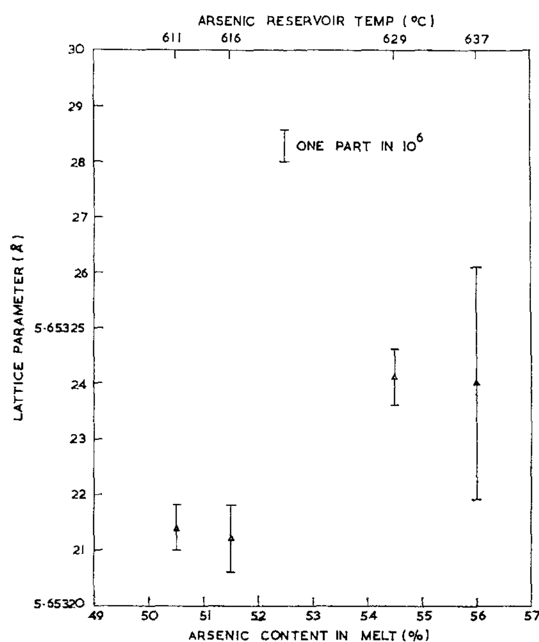

Figure 4 Effect of arsenic content in the melt on the lattice parameter of horizontally grown samples. The "error bars" give the measured limits of lattice parameter variation across the sample in question, and not the error of measurement.

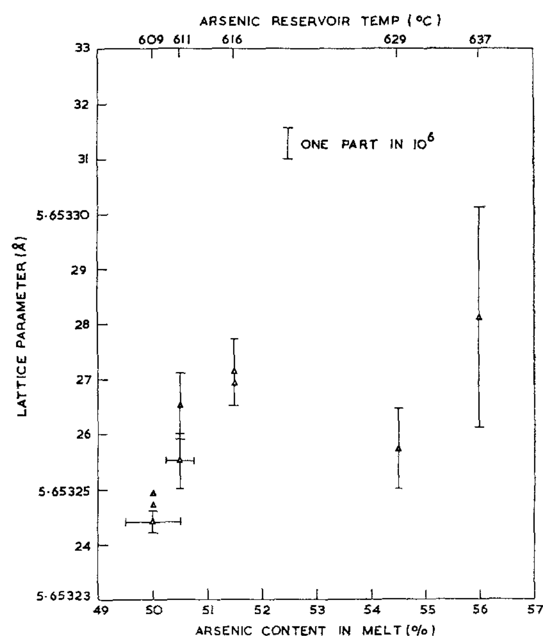

Figure 5 A repeat series of lattice parameter measurements on some of the samples in fig. 4.

measurements were made to avoid the procedure of closing the error loop [14] and between the two sets of measurements the experimental conditions had been altered, but the relative values confirm the increase of lattice parameter with arsenic temperature. It is also evident, from both figs. 4 and 5 that the non-uniformity of each sample, indicated by the "bar" at each point, increases with the arsenic content in the melt. This suggests that excess arsenic in the melt gives rise to inhomogeneities, perhaps by causing constitutional supercooling. The reasons for the lattice parameter variations across samples are being investigated in more detail.

4. Discussion

4.1. The Degree of Inhomogeneity revealed by Lattice Parameter Scans

An interesting outcome of the lattice parameter scans is the discovery of non-uniformity in lattice parameter across the samples. Although considerable variations across samples have been found, the material examined in this study is considerably more uniform than those quoted by Pierron and McNeely [15] who reported variations across samples of three parts in 10^5, two parts in 10^5 and one part in 10^5 for melt grown, liquid epitaxial and vapour epitaxial material respectively, compared with two parts in 10^6, one part in 10^5 and one part in 10^5 in the present work. Such inhomogeneities could be due to a number of causes such as variations in impurity concentration, degree of non-stoichiometry, dislocation density [18] or residual strain arising perhaps from stress during the growth or cooling of the crystals, but a satisfactory investigation of these variations must include an analysis of line profiles at various points across each sample. Such an analysis of line broadening was not undertaken in the present investigations. It might be possible to clarify the causes of inhomogeneity by means of rocking-curve experiments. Cohen and Focht [19] have found rocking-curve linewidths of about 6 sec (for the (444) reflection) for undamaged GaAs, which is approximately that predicted for perfect crystals. They also found rocking curve breadths of about 50 sec on the undamaged face of samples after grinding on the reverse face, this broadening was attributed to elastic strain. The dislocation densities observed in the present crystals by etch-pit techniques were of the order 10^4 to 10^5 cm^{-2}, which according to the relation of Kurtz, *et al* [20] could produce a broadening of from 2 to 6 sec which, if accompanied by a change in line shape, makes it

possible that these inhomogeneities are due to variations in dislocation density, but this is felt to be an unlikely explanation on present evidence. Variations in impurity content have also been revealed by electrical measurements, but are thought not to be sufficient to explain these observations, since the concentration required, from the experiments on heavily doped samples, would be of the order 10^{18} cm^{-3}, whereas concentrations indicated by the electrical measurements were less than 8×10^{16} cm^{-3}.

In addition to dislocations and dissolved impurities it is likely, from transmission electron microscopy evidence on similar material [21-27] that other crystallographic and impurity-type defects are present, the latter particularly in the heavily doped layers [21-24]. Defects such as dislocation loops, impurity clusters and precipitate particles, have been observed to vary in density on a macro-scale and might be the cause of the macro-variations in lattice parameter observed here. A further possibility is a varying degree of non-stoichiometry, suggested by the dependence of uniformity on arsenic pressure. Further investigations of the causes of inhomogeneities are proceeding.

4.2. Non-Stoichiometry in Gallium Arsenide

The variation of lattice parameter with arsenic pressure shown in figs. 4 and 5 provides strong evidence for the existence of non-stoichiometry on the arsenic-rich side of the gallium arsenide phase. Other possible explanations, in terms of variation in impurity concentration or dislocation density seem unlikely The maximum *n*-type carrier concentration in the samples of figs. 4 or 5 was 8×10^{16} cm^{-3}; while the results discussed in section 4.3 indicate that a concentration of order 10^{18} cm^{-3} would be required. A variation in dislocation density in these samples, which was reported by Brice [28] on similar samples, was only of the order of 10^4 cm^{-2}, although it cannot be ruled out until there is a systematic investigation of this parameter, seems unlikely as an explanation since it should produce a line-broadening of less than 2 sec [20].

A number of different defect models could possibly account for the observed effect of arsenic excess on the lattice parameter, which is of the same order but of opposite sign to the trend found by Straumanis and Kim [1] on powdered samples. The differences from the present work found in that investigation [1] might be associated with the higher susceptibility of powdered samples to contamination, although it is noteworthy that the effects of excess arsenic and gallium observed by Straumanis and Kim were reversible. These differences might also be associated with differences in temperature, since in Straumanis and Kim's investigation the samples were annealed at 1000°C, while the present samples might be expected to bear some relation to the situation existing at the melting temperature; it is not impossible that quite different defect equilibria exist at these two temperatures. A further possible reason for the discrepancy is that Straumanis and Kim used a 422 reflection in their study whereas the present work employed an 800 reflection. If the excess arsenic distorted the shape of the unit cell these results might not be inconsistent with those of the present work.

A notable feature of the present results is the fact that close agreement between the lattice parameters of undoped liquid epitaxy, vapour epitaxy and melt-grown material has been found. In particular, the lattice parameter values of solution-grown material and melt-grown material grown under gallium-excess conditions, were very close, although these were prepared at widely different temperatures which would be expected, on thermodynamic grounds, to be associated with different positions on the phase boundary. We may conclude, therefore, that either there is an extremely narrow phase extent on the gallium-rich side or else changes in stoichiometry occur during cooling.

The effect of point defects on the lattice parameter of gallium arsenide is uncertain theoretically, but the most likely defects will be discussed. The effect of a vacancy is particularly uncertain since it has different effects in covalent and ionic materials. Calculations by Mott and Gurney [29] and by Kurnick [30] have shown that a vacancy in an ionic crystal would be expected to expand the lattice by about 10%. In contrast, Swalin [31] has shown that a vacancy in silicon and germanium should *contract* the lattice. Vook [32] has suggested that a vacancy in III-V semiconductors should expand the lattice as in ionic solids but gives no justification for this. In a calculation for ZnS by Asano and Tomishima [33], in which covalency and ionicity both have a contribution, it is concluded that zinc vacancies should contract the lattice and sulphur vacancies expand it. There are some unsatisfactory points about this analysis, but in the absence of a rigorous theory in this particular

case, the same type of behaviour will be assumed for gallium arsenide. With this assumption the present results cannot be explained in terms of gallium or arsenic vacancies. The increase in lattice parameter with arsenic content thus suggests the following possible explanations, considering simple defects only:

(*a*) An increase in the density of arsenic interstitials, which might be expected to expand the lattice.

(*b*) An increase in the density of arsenic atoms on gallium sites (the effect of these defects on the lattice parameter is uncertain theoretically). Further deductions as to the identity and concentration of the defect or defects may be made using the lattice parameter and density method [34]. To enable this method to be applied, density measurements are being made on the present samples and will be reported in a future publication.

4.3. The Effect of Heavy Doping on the Lattice Parameter

The limited evidence presented in the paper indicates a large ($\sim 10^{-4}$) effect of heavy doping on lattice parameter. King [35] has pointed out that, in metals, the prediction of the sign of this effect from the relative atomic sizes is unreliable, but when the solute atom is larger than the solvent atom an increase in lattice parameter usually results, and he has emphasised the limited range over which Vegard's law is applicable. In covalent crystals the uncertainties are likely to be even greater since the use of the atomic radius concept in this context is rather questionable. However, in the absence of a more rigorous treatment, we will examine these results using the covalent (or Pauling) radii. There is evidence that tin atoms substitute for gallium in gallium arsenide [36] and using the values 1.26 and 1.40 Å for the covalent radii of gallium and tin respectively [36] an expansion of the lattice would be expected as was observed in sample LE6. This trend seems more reasonable physically than that observed using powder techniques by Kolm *et al* [37] who observed a decrease in lattice parameter with addition of tin. However, the smallest addition made in that study was 1 % (which corresponds to about 4×10^{20} atoms/cm^3) which is an order of magnitude higher concentration than used in this study. It is possible that effects of precipitation could account for the apparent lattice parameter decrease at high tin concentration.

A quantitative comparison of the present results with prediction from the covalent radii may be made using the following formulation of Vegard's law, which expresses the change in lattice parameter $\Delta a/a$ in terms of the atom fraction of tin $(N_{Sn})/(N_{GaAs})$.

$$\frac{\Delta a}{a} = K \frac{N_{Sn}}{N_{GaAs}} \tag{1}$$

where

$$K = \frac{4}{\sqrt{3}} \frac{(r_{Sn} - r_{Ga})}{a}$$

Thus using the observed parameter change of 10^{-3} Å

$$\frac{N_{Sn}}{N_{GaAs}} = 3.094 \times 10^{-3}$$

Now N_{GaAs} = No. of gallium arsenide molecules/cm^3

$$= 2.216 \times 10^{22}\ \text{cm}^{-3}$$

Therefore $N_{Sn} = 6.85 \times 10^{19}\ \text{cm}^{-3}$

This estimate is of the same order as that measured by electrical techniques on sample LE6 (viz. 1×10^{19} cm^{-3}). A similar calculation for sample LE5 assuming that tellurium atoms substitute for gallium leads to an estimated concentration of about 1.7×10^{20} cm^{-3}. If tellurium substitutes for arsenic, however, the estimate would be 6.8×10^{19} cm^{-3} which is again in order of magnitude agreement with the electrically active tellurium concentration. In view of the limited validity of Vegard's law, discussed above, the correlation between lattice parameter change and doping concentration in these two cases is considered to be reasonable.

The TEM work of Laister and Jenkins [26, 27] has indicated that layers doped with tellurium above about 10^{18} cm^{-3} contain plate-like defects considered to be rafts of tellurium substituting for arsenic in (1 1 1) planes. They suggest that this should produce an expansion in the lattice perpendicular to the gallium-tellurium layer; such a distortion of the lattice might be detected by the use of different reflection types. In the present results, however, the tellurium in such defects might be expected not to be electrically active and might account for the change in lattice parameter being larger than expected from the electrically active concentration. An explanation in terms of mismatch of the layers with the substrate is considered unlikely in view of the fact that the thicker layer (LE5, 100 μm)

showed a larger deviation from the undoped parameter than layer LE6 (23 μm thick).

5. Conclusions

(*a*) The existence of a limited phase extent of the gallium arsenide phase has been confirmed in single crystals grown under different arsenic pressures.
(*b*) The lattice parameter increased with arsenic excess in the melt, from 5.65324 to 5.65328 Å for arsenic reservoir temperatures of 609 and 637°C respectively; an opposite trend to that reported for powdered material.
(*c*) It is suggested that the more likely defects present in arsenic-rich material are arsenic interstitials or replacement defects.
(*d*) The effect of doping with tin and tellurium on the lattice parameter is in fair agreement with that predicted from their covalent radii.

Acknowledgements

This paper incorporates work carried out on a CVD contract and is published by permission of the Ministry of Defence (Navy Department). The authors are grateful to Dr J. B. Mullin (RRE, Malvern), J. C. Brice and M. J. King (Mullard Laboratories, Redhill), J. R. Knight (Allen Clark Research Centre, Plessey Co) and M. C. Rowland (SERL, Baldock), for the supply of gallium arsenide single crystals and layers. Useful discussions with Dr J. B. Mullin, Dr D. T. J. Hurle, Dr R. M. Logan, and T. W. Baker are acknowledged, and thanks are extended to Professor R. L. Bell for provision of laboratory facilities and for useful suggestions and encouragement.

References

1. M. E. STRAUMANIS and C. D. KIM, *Acta Cryst.* **19** (1965) 256.
2. B. K. CHAKRAVERTY and R. W. DREYFUS, *J. Appl. Phys.* **37** (1966) 631.
3. B. GOLDSTEIN and N. ALMELEH, *Appl. Phys. Letters* **2** (1963) 130.
4. J. BLANC, R. H. BUBE, and L. R. WEISBURG, *J. Phys. Chem. Solids* **25** (1964) 225.
5. M. FUJIMOTO, Y. SATO, and K. KUDO, *Jap. J. Appl. Phys.* **6** (1967) 848.
   F. A. CUNNELL and C. H. GOOCH, *J. Phys. Chem. Solids* **15** (1960) 127.
   L. J. VIELAND, *J. Phys. Chem. Solids* **21** (1961) 318.
   H. RUPPRECHT and C. Z. LE MAY, *J. Appl. Phys.* **35** (1964) 1970.
6. M. S. SELTZER, *J. Phys. Chem. Solids* **26** (1965) 243.
7. E. W. WILLIAMS and D. M. BLACKNELL, *Trans AIME* **239** (1967) 387.
8. E. W. WILLIAMS, *Solid State Communications* **4** (1966) 585.
9. M. TOYAMA, *Japanese J. Appl. Phys.* **8** (1969) 1000.
10. H. OTSUKA, K. ISHIDA, and J. NISHIZAWA, *ibid* **8** (1969) 632.
11. E. MUÑOZ, W. L. SNYDER, and J. L. MOLL, *Appl. Phys. Letters* **16** (1970) 262.
12. H. R. POTTS and G. L. PEARSON, *J. Appl. Phys.* **37** (1966) 5.
13. W. L. BOND, *Acta Cryst.* **13** (1960) 814.
14. T. W. BAKER, J. D. GEORGE, B. A. BELLAMY, and R. CAUSER, *Advances in X-ray Analysis* **11** (1968) 359.
    T. W. BAKER, J. D. GEORGE, B. A. BELLAMY, and R. CAUSER, Research Report, AERE-R5152.
15. E. D. PIERRON and J. B. MCNEELY, *Advances in X-ray Analysis* **12** (1968) 343.
16. R. E. HONIG, R.C.A. *Review* **23** (1962) 567.
17. J. VAN DER BOOMGAARD and K. SCHOL, *Philips Res. Rep.* **12** (1957) 127.
18. E. D. PIERRON, J. W. BURD, and J. B. MCNEELY, *Trans. AIME* **1** (1970) 639.
19. B. G. COHEN and M. W. FOCHT, *Solid-State Electronics* **13** (1970) 105.
20. A. D. KURTZ, S. A. KULIN, and B. L. AVERBACH, *Phys. Rev.* **101** (1956) 1285.
21. E. S. MEIERAN, *J. Appl. Phys.* **36** (1965) 2544.
22. M. S. ABRAHAMS, C. J. BUIOCCHI, and J. J. TIETJEN *ibid* **38** (1967) 760.
23. M. S. ABRAHAMS and C. J. BUIOCCHI, *J. Phys. Chem. Solids* **28** (1967) 927.
24. H. KRESSEL, F. Z. HAWRYLO, M. S. ABRAHAMS, and C. J. BUIOCCHI, *J. Appl. Phys.* **39** (1968) 5139.
25. H. KRESSEL, H. NELSON, S. H. MCFARLANE, M. S. ABRAHAMS, P. LE FUR, and C. J. BUIOCCHI, *ibid* **40** (1969) 3587.
26. D. LAISTER and G. M. JENKINS, *J. Mater. Sci.* **3** (1968) 584.
27. *Idem, Phil Mag.* **20** (1969) 361.
28. J. C. BRICE and G. D. KING, *Nature* **209** (1966) 1346.
29. N. F. MOTT and R. W. GURNEY, "Electronic Process in Ionic Crystals", Oxford (1940).
30. S. W. KURNICK, *J. Chem. Phys.* **20** (1952) 219.
31. R. A. SWALIN, *J. Phys. Chem. Solids* **18** (1961) 290.
32. F. L. VOOK, Proc. 7th International Conference on the Physics of Semi-coductors, Paris 1965.
33. S. ASANO and Y. TOMISHIMA, *J. Phys. Soc. Japan* **13** (1958) 1126.
34. A. J. BRADLEY and A. TAYLOR, *Proc. Roy. Soc.* **A159** (1937) 56.
35. H. W. KING, *J. Mater. Sci.* **1** (1966) 79.
36. C. HILSUM and A. C. ROSE-INNES, "Semiconducting III-V compounds" (Pergamon 1961).
37. C. KOLM, S. A. KULIN, and B. L. AVERBACH, *Phys. Rev.* **108** (1957) 965.

Received 23 December 1970 and accepted 19 June 1971.