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Phase Extent of Gallium Arsenide Determined by the Lattice Constant and Density Method

BY M. E. STRAUMANIS AND C. D. KIM*

University of Missouri at Rolla, Department of Metallurgical Engineering; Rolla, Missouri, U.S.A.

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The lattice constant of the homogeneous GaAs phase drops from 5·65326 Å (25 °C) at the left gallium-rich border to 5·65298 Å at the arsenic-rich right border of the phase. The phase extends at least from 49·998 to 50·009 at.% As. Owing to uncertainty in wavelength and Avogadro number, the extent of the phase may increase by 0·009 at.%. At the stoichiometric composition the GaAs phase is sound (with 4·000 molecules per unit cell); it has a lattice constant of 5·65321 ± 0·00003 Å at 25 °C and a thermal expansion coefficient $\alpha = 6{\cdot}4 \times 10^{-6}$. °C^{-1} between 15 and 65 °C. Its experimental density was 5·3176 ± 0·0026 g.cm^{-3} and the X-ray density 5·3169 g.cm^{-3} at 25 °C (5·3167, using the new X-ray units).

At the right side of the phase there are vacant sites in the Ga sublattice, and at the left side vacant sites in the As sublattice.

The compounds GaSb and InSb did not show any phase extent.

Introduction

More and more attention is paid to the study of the intermetallic compounds of the elements of the third and fifth groups of the periodic system of elements. The reason for this interest is the similarity of these compounds to germanium and silicon, the two best understood and most widely used semiconducting materials at the present time. This similarity begins with their structure: they all are cubic and the compounds have the zinc blende structure.

Although much work is done with GaAs, nevertheless there are no precise lattice parameter measurements with samples of an exactly (± 0·05 °C) controlled temperature. The thermal expansion coefficient is unknown as well as the extent of the GaAs phase and its soundness or perfection. The intention of the present article is, therefore, to expand our knowledge concerning the latter two points for which precise lattice parameter and density measurements are necessary.

Method and literature review

Köster & Thoma (1955) as well as Boomgaard & Schol (1957) studied the system Ga–As and the compound GaAs, which has a melting point of 1238 °C. The range of the GaAs phase in the diagrams is given in the form of a straight vertical line, meaning that the extent of the phase is very narrow. This, however, can be checked by making precise lattice parameter determinations with samples of a composition to the left and to the right of the vertical line. If there is a difference between the lattice parameters, the phase has a certain width.

The first lattice parameter determinations of GaAs were made by Goldschmidt (1926) who obtained 5·646 ± 0·002 Å (Gmelin, 1936). Gieseke & Pfister (1958) found a much more precise value of 5·6534 ± 0·0002 Å, and recently Ozolin'sh, Averkieva, Ievin'sh & Goryunova (1963) arrived at the value of $a = 5{\cdot}65315 \pm 0{\cdot}00010$ Å for GaAs at 25 °C.

GaAs samples

Samples were prepared from high purity materials: 99·999% gallium (which stayed liquid at room temperature even below 0 °C because of undercooling) and arsenic (Baker Co.), which was refined by sublimation in vacuum. Samples were also obtained from the Aluminum Co. of America (Alcoa, East St. Louis, Illinois) and from the Siemens Company (Erlangen, West Germany). The latter company provided two kinds of GaAs: a material very close to the stoichiometric composition (Sm. 1) and a GaAs sample grown from liquid gallium (Sm. 2). According to the spectrographic analysis furnished by the Siemens Company, the stoichiometric GaAs contained between 20 and 120 ppm silicon as an impurity.

In order to find the extent of the GaAs phase, three more samples were necessary: one with the gallium and two with the arsenic excess. Such samples were prepared from Sm. 1, which was finely ground and mixed with certain amounts of gallium (3·4 wt.%, Sm. 3) and of arsenic (3·5%, average of two, Sm. 4). The mixtures were put into small quartz tubes, which were evacuated (to 19 microns Hg), sealed, heated at 1000° in their whole length for 18 hours and furnace cooled. Subsequent lattice parameter determinations showed that the Alcoa sample also contained an excess of arsenic.

Lattice parameters and expansion coefficients

The X-ray powder patterns obtained with all the GaAs samples were very sharp even with Cr radiation ($k\lambda\alpha_1 = 2{\cdot}28503$ kX; the conversion factor into Å was

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1·00202). The lattice constants were calculated from one single back-reflection line 422α_1 which appeared under a Bragg angle of about 82·80° on the asymmetric films. The use of a single last line leads to the highest precision in such a case; application of extrapolation methods *decreases* this precision (Beu, Landstrom, Whitney & Pike, 1964; Straumanis, 1959, 1960). The exact angles were computed, after measuring the positions of the lines on these films with a comparator, by a method already described (Klug & Alexander, 1954; Azároff & Buerger 1958; Straumanis, 1963). The powder patterns were obtained at constant temperatures of the sample (±0·05 °C) in 10·0 increments in a precision camera 64 mm in diameter (Straumanis, 1963). The powder mounts had a thickness below 0·2 mm so that the absorption correction could be disregarded. To relieve the internal stresses introduced during grinding, the samples were annealed in vacuum at 400° for 1 hour. The refraction correction was added to the final results (Straumanis, 1955, 1959, 1960, 1963). The linear thermal expansion coefficients α were calculated from the a constants obtained at temperatures between 5 and 65 °C using the relation

$$\alpha = \Delta a / a \Delta t, \qquad (1)$$

where Δa is the difference in a constants at a temperature difference Δt.

The lattice parameters of three GaAs samples (Nos. 1, 2 and Alcoa) are plotted *versus* the temperature in Fig. 1. It follows clearly from the plot that the temperature expansion of the three samples is the same, a result which is not obtained when the precision of determination is lower. An expansion coefficient $\alpha = 6{\cdot}4 \times 10^{-6}$. °C^{-1} could be calculated from equation (1).

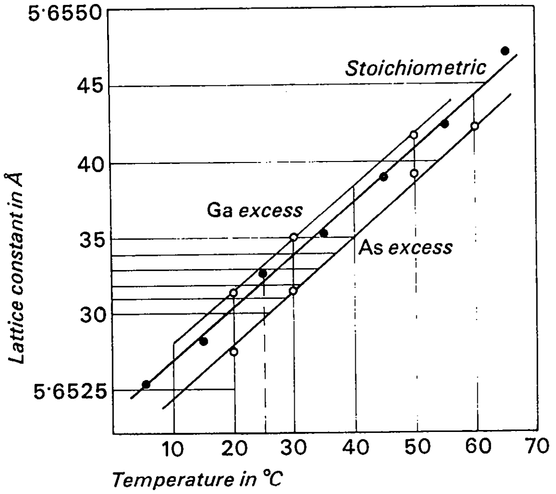

Fig. 1. Lattice parameters (Å) *versus* temperature of three GaAs samples. From top: Siemens (Sm. 2, Sm. 1) and Alcoa samples. Each point is an average of two powder patterns.

Using this expansion coefficient the constants found at various temperatures were reduced to a constant of 25·0 °C. In Table 1 the results of this reduction are shown for Sm. 1. The error calculated is the probable one s' (Straumanis, 1963). Fig. 1 shows further that the Alcoa sample has the lowest lattice constant of the three. The parameters of Sm. 3 and Sm. 4 were determined only at 25 °C. For comparison the lattice constants of all five samples are listed in Table 2, which shows that the Alcoa sample had within the limits of error the same lattice constant as sample 4, which was inhomogeneous. Therefore, the Alcoa sample had a slight excess of arsenic beyond the stoichiometric composition. However, a careful microscopic examination revealed that the sample was completely homogeneous. Hence, the composition of the Alcoa sample was close to that of the arsenic-rich border of the GaAs phase.

The lattice parameters of the inhomogeneous samples 2 and 3 with gallium excess also agreed within the limits of error. Therefore the width of the GaAs phase is represented by the drop of the lattice constant from 5·65325 at the gallium-rich to 5·65300 Å at the arsenic-rich side of the phase. Although the drop is only 0·00025 Å, it exceeds by far the precision of determination of the constants (±0·00003 Å) and is therefore real. The systematic errors, which are depressed to a minimum (Beu, 1963), using the asymmetric method, will not affect this difference. However, since Ozolin'sh *et al.* (1963) could not find any width of the GaAs phase, it seemed appropriate to repeat the measurements with newly prepared samples. To the Alcoa sample gallium was added and to the Siemens No. 2

Table 1. *Lattice constant a of Siemens No.* 1 GaAs, *with the refraction correction of* 0·00021 Å *added.* Cr α_1 *radiation*

Temperature	a_t Average	a_{25}
5·6 °C	5·65254 Å	5·65321 Å
15·0	282	318
25·0	327	327
35·0	353	317
45·0	390	318
55·0	425	317
65·0	472	328

Average at 25° 5·65321 ± 0·00003 Å

Table 2. *Lattice constants a of five* GaAs *samples at* 25 °C, *with the refraction correction of* 0·00021 Å *added*

All the samples were ground and heated at 400° (vacuum).

	Sample No.	a_{25}
(Siemens)	2 grown in liquid gallium	5·65326 ± 0·00002 Å
	3 with 3·4 % excess of gallium	5·65324 ± 0·00004
(Siemens)	1 stoichiometric, as received	5·65321 ± 0·00003
(Alcoa)	as received	5·65298 ± 0·00002
	4 with 3·5 % excess of arsenic*	5·65301 ± 0·00003

* Arsenic lines could be detected on the films.

sample, arsenic (99·999% pure). The heat treatment was the same as described. The lattice constant of Alcoa GaAs as received was remeasured. The results are summarized in Table 3. The newly determined lattice constants agree with those of Table 2 within the limits of error, confirming the drop in the constant by at least 0·00025 Å when arsenic is added to the GaAs rich in gallium; the reverse happens when gallium is added to the arsenic-rich phase.

The lattice constant of Sm. 1 is between the two limiting values and its composition should be very close to the stoichiometric. Sample 1 was also heated in vacuum at 800 °C. It sublimed partially. Nevertheless the lattice constants of the sublimed and rest parts remained within the span of 0·00025 Å between the two limiting values.

Density, perfection and phase extent of GaAs

In order to find the extent of the GaAs phase, the composition of the phase at its left and right borders had to be known. However, these compositions could not be determined by analysis because of two reasons: (1) samples 2, 3 and 4 contained an excess of gallium or of arsenic respectively; (2) the analysis of the homogeneous samples (No. 1 and Alcoa) had to be done with a precision which exceeded by far that attainable in our laboratory.

Therefore, for the estimation of the borders of the phase another method was used which proved to be successful in the case of TiO (Straumanis, Ejima & James, 1961). The actual number n' of GaAs molecules per unit cell is

$$n' = vdN_0/M \qquad (2)$$

where v is the volume of the unit cell, d the experimental density of the homogeneous crystalline substance, M its molecular mass and N_0 is Avogadro's number ($6{\cdot}0240 \times 10^{23}$). Assuming now that in the Alcoa sample the arsenic sublattice is completely filled up with As atoms, the value x of the non-stoichiometric compound $\mathrm{Ga}_x\mathrm{As}$ can be calculated from equation (2).

$$4x\mathrm{Ga} + 4\mathrm{As} = vdN_0 \text{ or } x = (vdN_0 - 4\mathrm{As})/4\mathrm{Ga} \qquad (3)$$

Precision density determinations are, however, necessary for the calculation of x. These could well be made with the large (9·1 g) Alcoa sample. At first the sample was checked microscopically using high magnification (oil immersion) for inhomogeneity and for the presence of microporosity. None could be detected. The sample, suspended on a fine tungsten wire, was weighed in air and xylene, the density of which was known. Taking into consideration the temperature, the density of the sample was calculated and reduced to vacuum. Ten determinations were made and the following values were obtained after reduction to 25 °C: 5·3165, 5·3160, 5·3153, 5·3156, 5·3152, 5·3156, 5·3156, 5·3160, 5·3154, and 5·3154. As an average 5·3157 g.cm^{-3} was calculated with a probable error of ±0·0003. There still might have been separate voids in the piece outside the sections examined by the microscope. To detect them, the large piece was trimmed, broken into smaller and the density of each of the four pieces obtained was determined separately. It agreed within the limits of error with the density of the unbroken piece.

Using this value, and the lattice constant from Table 2, $x = 0{\cdot}99964$ was calculated for $\mathrm{Ga}_x\mathrm{As}$ at the right border of the phase, which corresponds to a composition of 49·991 at.% Ga and 50·009 at.% As. The determination of the composition of $\mathrm{Ga}_x\mathrm{As}$ at the left border of the phase was also an estimation, because the density of the stoichiometric sample 1 could not be found with sufficient precision owing to its small size (1·4 g): a density of $5{\cdot}3176 \pm 0{\cdot}0026$ g.cm^{-3} at 25 °C was obtained. Nevertheless, this value differed only slightly from the X-ray density $D_x = 5{\cdot}3169$, calculated for the same sample from equation (1), using the respective lattice constant, the molecular mass (based on $\mathrm{C} = 12$) of stoichiometric GaAs, and assuming that $n = 4{\cdot}0000$. Thus, the close agreement between the X-ray and the experimental density of Sm. 1 testifies that it has a nearly stoichiometric 50–50 composition.

Since the lattice constants of these two samples are also known the left border of the phase can be found by extrapolation (to 5·65326 Å of the GaAs saturated with Ga), as shown in Fig. 2.

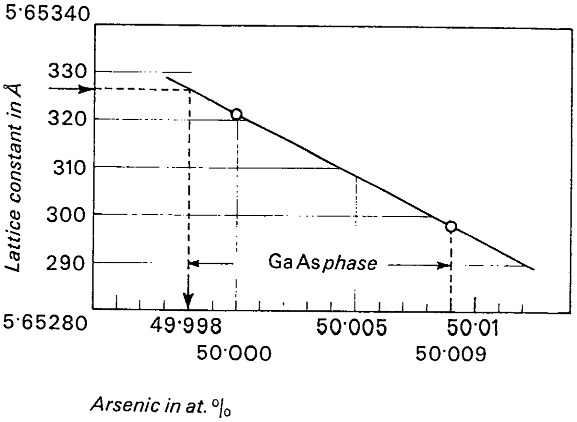

Fig. 2. Extent of the GaAs phase. Left: the gallium-rich border of the phase is found by extrapolation.

Table 3. *Redetermination of a of the* GaAs *samples*

(See Table 2)

Sample compositions	a_{25}
Alcoa + 50% gallium (excess)	5·65329 Å
Alcoa as received (new powder mount)	5·65299
Siemens No. 2 (slight excess of gallium) + 10% arsenic	5·65297

From Fig. 2 it can be read that the homogeneous phase extends from 49·998 to 50·009 at.% As with the stoichiometric composition close to the left border. However, while the present article was under review, the book by Bearden (1964) appeared, in which it is shown that the conversion factor from kX to Å should be $\Lambda = 1{\cdot}002056$. The respective Avogadro number N is then calculated from

$$N\Lambda^3 = 6{\cdot}05972 \times 10^{23}$$

(Bearden, 1964) and $N = 6{\cdot}0225 \times 10^{23}$ g.mol^{-1} is obtained. Using the new Å units, the new Avogadro number, the densities determined and equation (3), the GaAs phase extent of 0·011% widens by additional 0·009 at.%. Thus, because of uncertainty in the wavelengths and of the Avogadro number, the phase extent may lie between 49·998 to 49·997 at.% As on the left and 50·009 to 50·017 at.% As on the right side of the phase. The uncertainty due to experimental errors is estimated to be at the gallium-rich side ±0·001, and at the arsenic-rich side ±0·005 at.%. The new X-ray density of the sample of nearly stoichiometric composition (Siemens No. 1) then becomes 5·3167 as compared with 5·3169 g.cm^{-3} calculated with the old units.

Conclusions

A sure indication that the GaAs phase has a certain extent is the drop in lattice constants when passing from the left to the right side field of the phase. Ozolin'sh *et al.* (1963) could not detect this difference, because their precision of determination was lower (±0·00010 Å), although the line sharpness on the GaAs patterns is the same or even better than in the case of InAs, the *a* measurements of which they reported with a precision of ±0·00005 Å. This indicates that they had GaAs samples with slightly varying *a* constants caused by the phase width of GaAs. The GaAs phase may extend slightly beyond 50·009 or 50·017 at.% As respectively. There was no possibility to check this, because small amounts of a second phase cannot be detected by etching and microscopic technique. Since an addition of about 3% arsenic beyond the composition of GaAs (see Table 2) caused the appearance of arsenic lines on the powder patterns the phase could not contain considerably more than 0·009 to 0·017 at.% excess arsenic.

This investigation reveals further that, because of the close equality of X-ray and macroscopic densities, the structure of the stoichiometric GaAs is perfect or sound with 4·0000 molecules per unit cell. Consequently, going to the right side of the phase, the number of vacancies in the gallium sublattice increases (excess of arsenic) and *vice versa*, the number of vacancies increases in the arsenic sublattice (excess of gallium) approaching the left side of the GaAs phase. A similar behavior displayed the Ti_2O_3 phase (Straumanis & Ejima, 1962).

However, investigations made with the intermetallic compounds GaSb and InSb showed no indications for a phase width beyond the limits of error.

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