Study of the Phase Diagram of the GaAs-GaSb Quasi-Binary System*

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A study has been carried out on the quasi-binary phase diagram between GaAs and GaSb compounds, both of which crystallize in the zinc-blende structure. The liquidus and eutectic temperatures were determined by means of differential thermal analysis. Microscopic structures of several alloys were found to consist of primary crystals of the GaAs compound and an eutectic mixture of the GaAs and GaSb compounds. X-ray diffraction profiles indicated that an alloy containing 30 mol% GaAs consists of GaAs and GaSb phases, whose lattice parameters are slightly different from those of the stoichiometric compositions. Thermodynamic calculations were also carried out by using some data determined by the present experiment.

These results lead to the conclusion that this quasi-binary system is an eutectic type, whose eutectic point occurs at 3.0 mol% GaAs at 708°C. Each mutual solid solubility was found to be 0.14 mol% GaAs and 1.24 mol% GaSb at the eutectic temperature.

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I. Introduction

A number of the III–V quasi-binary phase diagram have been studied previously, because such diagrams are very important in considering the properties of the III–V compounds and their preparations. If a complete solid solution is formed in such a system, semiconducting properties such as energy gap and carrier mobility change continuously. When a complete mutual solid solubility is not realized, knowledge of the solubility limits is very important to investigate the nature of the chemical bond in the system.

In the GaAs–GaSb system Müller and Richard[1] have found that the two compounds are mutually soluble in all portions. Recently Clough and Tietjen[2] have grown alloys of $GaAs_{1-x}Sb_x$ with compositions ranging from 1 to 80 mol% GaAs as well as GaSb by using a vapor phase epitaxial growth technique. On the other hand, Folberth et al.[3] have denied the existence of a complete range of solid solutions in this system.

The purpose of this paper is to determine the equilibrium phase diagram of the GaAs–GaSb quasi-binary system by means of differential thermal analysis, microscopic observation, and measurements of lattice constants by the X-ray method.

II. Experimental

1. Differential thermal analysis

Ga, As and Sb with purities better than 99.999% were used in this work. The required amounts of GaAs and GaSb which were prepared in advance were weighed out and sealed under vacuum into fused silica capsules ($11.5\phi \times 34$ mm) with a hole for the thermocouple as shown in Fig. 1 (a). The fused silica capsules were immersed in HF solution for 20 min, washed with water and then dried. The differential thermal analysis cell was placed in an inconel block ($350\phi \times 560$ mm) with two holes for the differential thermocouples. The inconel block was covered by a lid made of the same material to maintain the constant temperature as shown in Fig.1 (b). In order to melt the alloy constituents completely, the inconel block and the thermal analysis cell were heated to 1270°C higher than the melting temperature of the GaAs compound (1238°C). After holding at that temperature for 30 min, the specimen was cooled gradually at a constant cooling rate of 1.5°C per min.

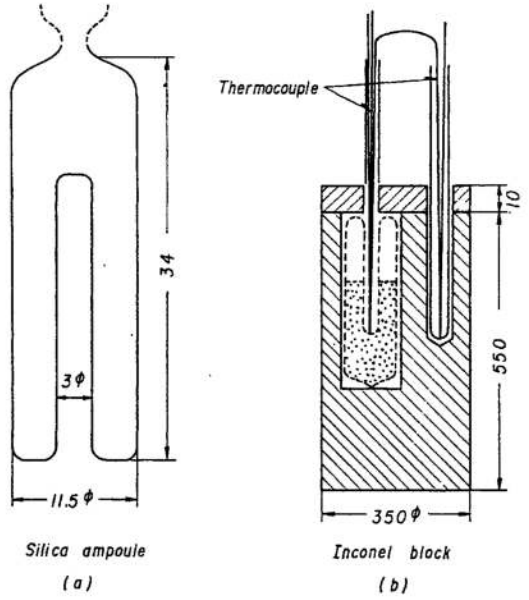

Fig. 1 Apparatus for thermal analysis.

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(1) E. K. Müller and J. L. Richards : J. Appl. Phys., 35 (1964), 1233.

(2) R. B. Clough and J. J. Tietjen : Trans. Met. Soc. AIME, 245 (1969), 583.

(3) O. G. Folberth and H. Welker : J. Phys. Chem. Solids, 8 (1959), 14.

The difference in temperature between the specimen and the inconel block was amplified by about 30 times and then registered by an X–Y recorder. Transformation temperatures determined from the cooling curves seem to be reasonably accurate since the temperature difference between the specimen and the inconel block was kept as small as within several degrees centigrade. Nominal compositions of the specimens are shown in Table 1.

Table 1 Nominal compositions of alloys and results of thermal analysis

Nominal compositions of alloys (mol% GaAs)	1.0	10	20	35	50	70
Liquidus temperature (°C)	773	919	959	1067	1101	1163
Eutectic temperature (°C)	703	708	702	708	705	703

2. Microscopic observation

Microscopic observation was carried out to determine whether the two compounds are mutually soluble in all portions or the miscibility in the solid state has a certain limit. A slow cooling rate and a prolonged homogenization of the specimens for microscopic observation were adopted to realize a condition near equilibrium. Etching was not needed, since the structural details were revealed immediately after polishing because of the difference in hardness among the constituents.

3. Determination of lattice parameters

Lattice parameters of the specimens used for thermal analysis were determined by using a Norelco diffractometer. In this case, it is noted that the relative values of lattice parameters are important. Peaks of diffraction lines were measured within the accuracy of about 0.008° in the range of 2θ from 100° to 160° after calibration by using the standard angles of Si powder. Average values of lattice parameter were calculated from the peaks corresponding to (440), (531), (620), (533), (444) and (511) of GaAs, and (620), (533), (444), (511), (642) and (553) of GaSb.

III. Results and Discussion

Typical cooling curves are shown in Fig.2. Two distinct deflection points are observed for the GaSb–10 mol% GaAs specimen. The first deflection point corresponding to the liquidus temperature is found to be at 919°C. The eutectic temperature is determined to be at 708°C from the second deflection point which is a little lower than 712°C, the melting point of GaSb. Table 1 shows the results of thermal analysis together with nominal compositions of the alloys. From the results, an eutectic type diagram with an eutectic temperature of 708°C was obtained as shown in Fig. 3.

Photos. 1 and 2 are typical photomicrographs, which show the distribution of primary crystals of GaAs and an eutectic mixture of GaAs and GaSb crystals. A GaSb–50 mol% GaAs alloy of Photo. 1 cooled very slowly to 740°C after melting, held at the temperature for 2 hr,

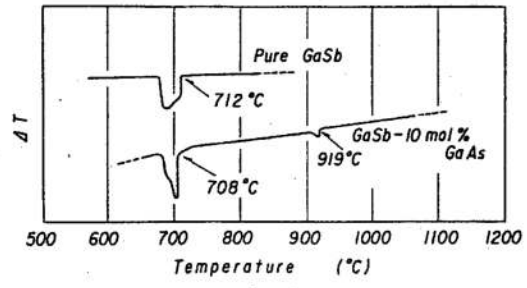

Fig. 2 Typical cooling curves.

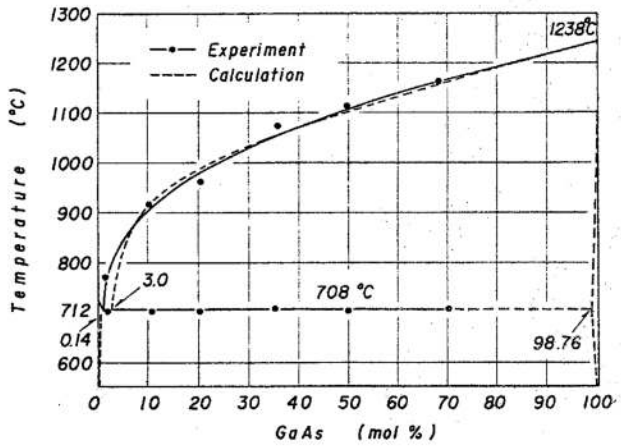

Fig. 3 GaAs-GaSb phase diagram.

Photo. 1 Photomicrograph of GaSb-50 mol% GaAs alloy. (×200)

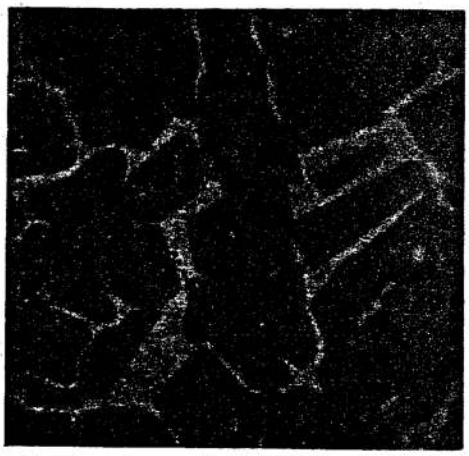

Photo. 2 Photomicrograph of GaSb-70 mol% GaAs alloy. (×200)

cooled to room temperature, and again homogenized at 630°C for a long time and then quenched into water. Photo. 2 shows a photomicrograph of a GaSb–70 mol% GaAs specimen used for thermal analysis, in which the quantity of the primary crystals of GaAs is richer than in the specimen of Photo. 1. From the above results, it is almost certain that this quasi-binary system is an eutectic type, and not a complete solid solution type.

The following result is thought to be decisive evidence to show the presence of a limited miscibility in the solid state in this quasi-binary system. The lattice parameters obtained by the method mentioned above are 6.0983 $\pm$ 0.0002 Å for the GaSb and 5.6544 $\pm$ 0.0002 Å for the GaAs compound respectively. Figure 4 shows X-ray diffraction curves for GaAs, GaSb and a quasi-binary alloy,

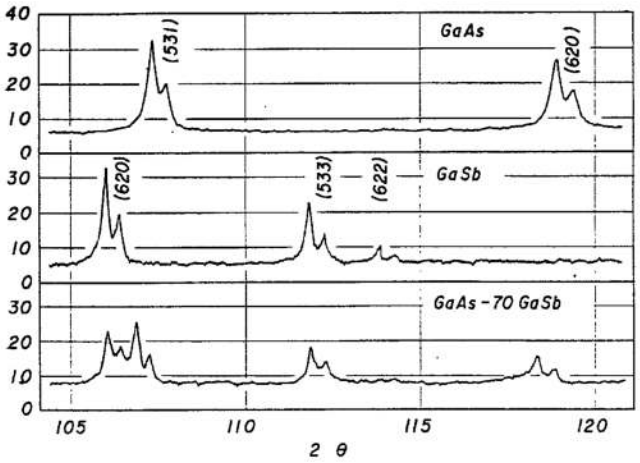

Fig. 4 Intensity distribution of diffraction lines in GaAs, GaSb and GaSb-30 mol% GaAs alloy.

as an example of a GaSb–30mol% GaAs alloy. The diffractometer tracings for the alloy is shown to consist of GaAs and GaSb crystals, whose peaks shift slightly from those of the stoichiometric compounds. An average value calculated from several peaks was taken to be the lattice parameter of the alloys in the same way as in the case of the stoichiometric compounds. In the case of a GaSb–30 mol% GaAs alloy, for instance, the lattice parameters of the two phases were estimated to be 6.0977 $\pm$ 0.0003 and 5.6597 $\pm$ 0.0004Å respectively. The solubility limits were determined from the lattice parameters of the two phases by assuming that the change in lattice parameter with composition obeys Vegard's law. The solubility limits thus calculated were found to be 0.14 $\pm$ 0.06 mol% GaAs and 1.24 $\pm$ 0.09 mol% GaSb respectively. It is very interesting that the solubility of GaSb in GaAs is about ten times larger than that of GaAs in GaSb. From the above result, it is apparent that there is a miscibility gap in this quasi-binary system, and its compound components have a small solid solubility.

In the next place, let us make some thermodynamic calculations from the present data to discuss the solid solubility and the eutectic composition. Since the stoichiometric compounds are easily formed between III and V elements because of their large binding energy, the molecular pair model[4] may reasonably be applied to the GaAs and GaSb quasi-binary systems, and thus the binary solution is taken to be regular.

Consider the condition of equilibrium between solid and liquid phases in the A–B binary system. Under the assumption of regular solution, the condition in which the chemical potentials must be equal in the two phases is represented as follows:

$$\Delta G_{f\mathrm{A}} + RT\ln x^l + \Omega^l(1-x^l)^2 = RT\ln x^s + \Omega^s(1-x^s)^2, \quad (1)$$

$$\Delta G_{f\mathrm{B}} + RT\ln(1-x^l) + \Omega^l(x^l)^2 = RT\ln(1-x^s) + \Omega^s(x^s)^2. \quad (2)$$

where ΔG_f is a change in the free energy of fusion, Ω a quasi-chemical interaction energy, x^l and x^s the mol fraction of liquid and solid phases, respectively.

Similarly, the condition of equilibrium between the two solid phases, α and β, is represented as follows:

$$RT\ln x^\alpha + (1-x^\alpha)^2(D+2x^\alpha E) = RT\ln x^\beta + (1-x^\beta)^2\{D+2x^\beta E\}, \quad (3)$$

$$RT\ln(1-x^\alpha) + (x^\alpha)^2\{D+(2x^\alpha-1)E\} = RT\ln(1-x^\beta) + (x^\beta)^2\{D+(2x^\beta-1)E\}. \quad (4)$$

In the above equations, the concentration dependence of interaction energy for the solid phases is considered as $\Omega^s = D + Ex$, where x is the mol fraction of each phase and D and E are constants. The value of Ω^s was estimated to be $8670 + 4230\,x$ cal/mol from eqs. (3) and (4) by using the experimental data of 1.24 and 0.14 mol% for x^α and x^β respectively.

The eutectic composition and the interaction energy for the liquid phase can be evaluated from eqs. (1) and (2) to be 3.0 mol% GaAs and -1470 cal/mol respectively. Table 2 shows the values for x^l and x^s calculated

Table 2 Calculated values for x^l and x^s

Temperature (°C)	x^l (mol% GaAs)	x^s (mol% GaAs)
919	10	99.37
1101	50	99.78
1163	70	99.90

from eqs. (1) and (2). The proposed phase diagram of the GaAs–GaSb quasi-binary system is shown in Fig. 3. There seems to be good agreement between the experimental and the calculated liquidus curves, shown with the solid and the dashed line respectively, except near the eutectic temperature. For example, the calculated value for the composition of the solid equilibrated at 1163°C with the liquid of 70 mol% is 99.90 mol% GaAs. This is consistent with the experimental result that the crystallized GaAs has only a very low solubility for the GaSb phase. On the other hand, for the solid-solid equilibrium, the solid solubility of GaAs in GaSb at 600°C is evaluated to be 0.092 mol% GaAs. It may be necessary to take account of a vibrational entropy for a more exact estimation.

The present phase diagram is in disagreement with

(4) K. Osamura and Y. Murakami : Japan. J. Appl. Phys., 8 (1969), 967.

the existence of a complete range of solid solutions proposed by Müller et al. and Clough et al. The discrepancies seem to be due to the different experimental conditions. The present experiment was based on thermal analysis of the alloys prepared by melting which is the usual method for studying an equilibrium phase diagram, while they used a technique which is thought to be far from an equilibrium condition.

IV. Summary

The quasi-binary phase diagram of GaAs and GaSb compounds has been investigated by means of differential thermal analysis, microscopic observations and X-ray measurements of lattice parameters. Thermodynamic calculations were also carried out by using the data obtained by the present experiment.

From these results it has been concluded that this quasi-binary system is a simple eutectic type, with its eutectic point at 3.0mol% GaAs at 708°C. The solid solubilities in both terminal solid solutions are found to be 0.14 mol% GaAs in GaSb and 1.24 mol% GaSb in GaAs respectively.

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