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Abstract

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Chemistry

The initial binary substances of the pseudobinary section AlSb–GaSb of the ternary system Al–Sb–Ga are semiconductors of the type A^III B^V, to whose properties an extensive literature is at present devoted. The possibility of the formation of homogeneous regions in alloys of substances of this type is of interest from the standpoint of obtaining semiconductors with a combination of electrical and physicochemical properties more advantageous for practical purposes than in binary compounds.

According to the data of Köster and Thoma, who investigated the system AlSb–GaSb, as well as the systems AlSb–InSb and GaSb–InSb, there is no appreciable mutual solubility of the binary components in the solid state in them, and the systems are treated as eutectic ones (^1).

One of the authors of the present work, together with N. N. Fedorova and I. E. Gorshkov, studied the system GaSb–InSb and also made an orientational study of the system AlSb–InSb (^2, ^3). As a result, in contrast to the data of Köster and Thoma, mutual solubility of the binary components over a wide concentration interval was found in these systems. These works made it possible to reveal the main feature of these systems, consisting in the presence of a tendency toward the formation of nonequilibrium states in connection with the pronounced covalent type of interaction between the atoms of these substances.

Apparently, the latter circumstance was not taken into account by Köster and Thoma, which led them to the erroneous conclusion that solid solutions were absent in the systems AlSb–InSb and GaSb–InSb. As for the system AlSb–GaSb, as a result of preliminary experiments one of the authors suggested that solid solutions also exist in this system.

In the present work, the results of a physicochemical investigation of this system are presented, confirming this supposition.

The substances studied were prepared by fusing the initial simple substances in graphite crucibles in an argon atmosphere. As in the work of Köster and Thoma, alloys were prepared with ratios of the initial binary components of 1 : 4, 1 : 1, 4 : 1, and also the compounds themselves—gallium antimonide and aluminum antimonide. To study the nature of the interaction of the substances in these alloys, the following methods were used: thermal analysis, examination of the microstructure and microhardness, and investigation of the distribution of electrical conductivity along the ingot. We did not use the X-ray method, since preliminary experiments showed that this method is ineffective because of the great closeness of the lattice periods of the given compounds.

Thermal analysis was carried out on a Kurnakov pyrometer. Substances in amounts of about 7 g were sealed in evacuated Stepanov quartz vessels. The rate of heating and cooling in the experiments was 10–15° per minute. Both simple curves and differential curves were recorded.

The microhardness was determined on a PMT-3 instrument; the surface of the specim—

The MOV was preliminarily etched with a 5% solution of ferric chloride in hydrochloric acid in a ratio of 1 : 2.

The distribution of electrical conductivity along the ingot was determined by the usual probe method.

Investigation of the substances immediately after synthesis revealed a pronounced compositional inhomogeneity. Thus, the heating and cooling curves gave results coinciding with those of Koster and Thoma. The structure of the substances was fine-crystalline; the microhardness showed a considerable scatter of values both within the grains and between them.

The electrical conductivity also showed a large scatter of values along the ingot.

For homogenization of GaSb—InSb alloys in previous works ([2,3]), prolonged annealing of the substances in powder form was used at temperatures close to the melting temperature of the more fusible binary component. This method, in addition to its long duration, also has the disadvantage that substances in powder form cannot be used for studying electrical properties or for fabricating a definite type of semiconductor device. Therefore, in the initial period of the investigations, for homogenization of the alloys we used a method of annealing ingots in the form of pieces in vacuum at a temperature of 600° for 2000 hours. However, the annealing gave no noticeable positive results.

Subsequently, another method was used for homogenizing the alloys, namely, zone leveling. We chose this method for the following reasons. Substances of type $A^{III}B^{V}$ are, by the nature of their chemical bonding, very close to the semiconductors—elements of group IV. We therefore assumed that alloys of type $A^{III}B^{V}$—$A^{III}B^{V}$ could be homogenized by the same procedure as silicon and germanium alloys ([5]).

Zone leveling was carried out by the usual method, with the heater being moved successively in opposite directions at a rate of 9—10 mm/hr, with an initial total ingot length of 25 cm and a width of the molten zone of 3—4 cm. The temperature in the molten zone corresponded to the temperatures of the liquidus points of the diagram of Koster and Thoma (^{1}). After twenty passes of the zone, the middle part of the ingot, 6–8 cm long, was investigated.

Study of the microstructure of the samples showed that they were coarse-crystalline, with grain sizes up to 1 mm, and that they had no inclusions (of eutectic or other character). The scatter of microhardness and electrical conductivity along the length became considerably smaller, and the microhardness in alloys of this system had a maximum at a composition of 1 : 1 (AlSb · GaSb).

Before the alloys were studied by thermal analysis, their chemical analysis was carried out at our request by T. V. Cherkashina, to whom the authors express their sincere gratitude. The analysis showed a tendency toward some transfer of the more fusible compound in the direction of zone motion. Therefore, the compositional data given below in considering the results of thermal analysis may have some deviations toward an increased amount of the more refractory compound—aluminum antimonide.

Thermal analysis of the alloys of the system gave results sharply differing from the data of Koster and Thoma. In Fig. 1 are plotted the data obtained both by us and by the aforementioned investigators. The data obtained by us indicate that, in the system under study, the interaction of the binary components under conditions approaching equilibrium does not have a eutectic character, but leads to the formation of solid solutions over a wide concentration range. It proved very convenient to use zone leveling before thermal analysis, which, as far as we know, had not previously been used by anyone.

Samples of the alloys after zone melting were left in air for a long time for the purpose of qualitatively comparing their behavior

with the behavior of aluminum antimonide, which, as is known, decomposes in air. It turned out that with an increase in the content of gallium antimonide in the alloys they become increasingly stable with respect to the action of air of ordinary humidity. Particularly stable (over the course of 2 months no changes in the polished surface were observed) were samples containing more than half gallium antimonide.

Further, it is necessary to investigate the phase diagram more fully with a larger number of alloys. It is possible that with more perfect homogenization the solidus line will rise somewhat. Nevertheless, the data obtained unambiguously resolve the question of the nature of the interaction of the components in this system: in it, undoubtedly, the formation of solid solutions takes place over a wide concentration range. Bearing in mind the features of the structure and type of bonding of these substances, as well as the nature of the change in microhardness, it may be asserted that these solutions are substitutional solid solutions. We assume that the alloys of this system will have practical importance, since the combination of physicochemical and electrical properties in them should be considerably more favorable than the combination of the same properties in the original binary compounds.

Fig. 1. Quasibinary section AlSb—GaSb: a—according to Kester and Thoma, b—according to our data

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The fact of the formation of substitutional solid solutions in the pseudobinary section AlSb—GaSb of the ternary system Al—Sb—Ga, together with the data on the systems GaSb—InSb and AlSb—InSb investigated earlier (2,3), makes it possible to remove the contradiction noted by some authors (6,7) in connection with discussion of the data of Kester and Thoma. This contradiction consists in the fact that in systems of the same type with substituting components sharply different in all characteristics (GaP—GaAs and InP—InAs), substitution occurs, whereas in the AlSb—GaSb system, where the substituting components are close, it does not occur.

Using our data, we have the possibility of interpreting the formation of substitutional solid solutions in substances of type $A^{III}B^{V}$ from a single point of view, comparing the electrostructure constants of the substituting elements (9). The electrostructure constant—a characteristic introduced by B. V. Nekrasov (8)—gives an idea of the energy of the cores of the substituting elements. The use of precisely this characteristic corresponds to the concept of the bond model in substances of this group (9).

The material available up to the present time on substitutional solid solutions in systems of the type mentioned is summarized in Table 1.

Table 1

Systems	Nature of interaction	Electrostructure constants of the substituting elements, kcal/mol	Difference of constants, % relative to the smaller value	Source
GaSb—InSb	Dissolution over a wide concentration range	705—644	9.4	(2,3)
AlSb—InSb	Dissolution over a wide concentration range	653—644	1.4	(3)

Systems	Nature of interaction	Electrostructure constants of the substituting elements, kcal/mol	Difference of constants, % relative to the smaller value	Source
AlSb–GaSb	Dissolution over a wide concentration range	653–705	8.0	Present work
GaAs–InAs	Dissolution over a wide concentration range	705–844	9.4	([2])
GaP–GaAs	Dissolution over a wide concentration range	1490–1433	3.6	([7])
InP–InAs	Dissolution over a wide concentration range	1490–1438	3.6	([7])
GaAs–GsSb	Absence of dissolution over a wide concentration range	1438–1278	12.4	([2])
InAs–InSb	Absence of dissolution over a wide concentration range	1438–1279	12.4	([2])

Consideration of the data in Table 1 makes it possible to conclude that the formation of solid solutions of substances of the type $A^{III}B^{V}$ over a wide range of concentrations occurs when the relative difference in the electrode constant of the substituting elements does not exceed 9.4%.

Undoubtedly, in addition to this principal factor, the substitution process may also be influenced by the chemical nature of the element being substituted, the purity of the materials used, etc.

N. K. Takhtareva and A. S. Borshchevskii took part in the experimental part of the work.

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