

LOW TEMPERATURE SYNTHESIS OF III-V SEMICONDUCTOR COMPOUNDS

E.P. Trifonova, N.N. Zheleva and D.B. Kushev

Semiconductor Physics and Technology Research Laboratory  
University of Sofia, Bd. A. Ivanov 1, 1126 Sofia, Bulgaria

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ABSTRACT

Direct low temperature synthesis was applied for preparing III-V compounds. Its major advantages are: the purity of the product is determined by that of the initial elements; the vapor pressure of the group V element is reduced.

MATERIALS INDEX: gallium, arsenides, antimonides, indium

Introduction

The synthesis of pure compounds is an essential step in the preparation of semiconductor bulk crystals and epitaxial layers. The conventional high temperature synthesis consists in a direct interaction of elements in evacuated quartz ampoules at temperatures which exceed the melting points of the binary compounds by 50 - 100 K. In the case of low volatility of the components, the synthesis of the compound, such as GaSb and InSb, may be carried out in inert (e.g., hydrogen) atmosphere. In general, the method may be applied to the synthesis of congruently melting substances and substances of low dissociation pressure and/or low volatility of the elements. With the exception of InSb, the III-V compounds melt at temperatures higher than 700°C and during the synthesis a great possibility exists of their contamination due to interaction with the ampoule and the gases diffusing through it.

The low temperature methods are usually indirect: the elements interact in a medium of a solvent (a melt of an element or a compound). A substantial advantage of these methods is the significant decreasing of synthesis temperatures, in some cases by several hundreds of degrees below the melting point of the compound. An example is the diffusion-controlled synthesis in solution (synthesis, solute diffusion (SSD) method), used mainly for preparation of phosphides (GaP, InP) at relatively low temperatures. Recently, the SSD method was applied to the synthesis of high purity GaAs (1). The temperature of the gallium melt, from which the polycrystal product precipitates out, is 930°C.

A very important disadvantage of the upper temperature methods is the necessity of separating the solvent from the system after the synthesis has been carried out. The prepared semiconductor compound is inevitably doped by the solvent (for instance, InAs is doped with iodine during its preparation in InI<sub>3</sub>-medium (2)).

It is evident that an optimal synthesis method would be a low temperature direct interaction based on the combination of the indirect methods low temperature and the approach of the direct high temperature method. Such a low temperature direct synthesis was proposed for CdTe (3) and other binary tellurides and selenides (4).

By this method we have prepared some binary chalcogenides and solid solutions (5) which have not been synthesized in (4).

In this work we present the preparation of III-V compounds by direct low temperature synthesis. As far as we know, this is the first application of the method to III-V compounds.

### Synthesis and Results

Equimolar quantities of the elements from IIIA and VA groups of the periodic system are evacuated and closed in an outgassed quartz ampoule. The mixture is heated for several days at temperatures in the interval from 400 to 650°C (6). The compound is identified by X-ray phase analysis. The completeness of the interaction is evaluated by the presence and the quantity of additional phases.

As an example, we are giving here the conditions for the synthesis of GaAs: the initial mixture contained 0.04 mol Ga and 0.04 mol As; it was closed in a quartz ampoule at  $\sim 10^{-4}$  Pa; the synthesis temperature was  $580 \pm 20^\circ\text{C}$ ; the duration was 140 h. The X-ray phase analysis confirmed the preparation of a cubic, zinc-blend structure type material with a lattice parameter of  $a = 5.6525(5) \text{ \AA}$  (Fig. 1). A second phase was not detected. The yield was 0.04 mol GaAs (100% interaction). Figure 2 is a scanning electron micrograph of the as-synthesized material.

InAs, InSb and GaSb were synthesized at similar conditions (Table 1). It can be seen that the synthesis temperatures are significantly lower than the melting points of the compounds.

When AlSb (0.05 mol) was synthesized at  $\sim 640^\circ\text{C}$ , a 50% completeness of the interaction was achieved for  $\sim 100$  h. The process presumably is delayed by the layer of  $\text{Al}_2\text{O}_3$  on the surface of Al, preventing its interaction with Sb. It is known that this is a specific difficulty in processes involving Al.

When InP (0.02 mol) was synthesized at  $\sim 420^\circ\text{C}$ , a 20% interaction was reached for  $\sim 300$  h. Here the synthesis temperature was limited by the vapor pressure of phosphorous:  $\sim 1$  atm at  $\sim 420^\circ\text{C}$ . Provided thick-walled quartz ampoules were used, the synthesis temperature could be increased up to  $\sim 500^\circ\text{C}$ , which would result in a more complete interaction.

In order to verify the possibility of applying the method to the preparation of solid solutions of III-V compounds, we tried to prepare a quasiternary solid solution GaSb-InSb-AlSb. The composition of the initial charge corresponded to the solution  $\text{Ga}_{0.90}\text{In}_{0.06}\text{Al}_{0.04}\text{Sb}$  (0.08 mol); the temperature was  $\sim 600^\circ\text{C}$ ; the duration was  $\sim 120$  h. The X-ray analysis showed that a cubic, zinc-blend structure type material was prepared with  $a = 6.105 \text{ \AA}$ . The completeness of the interaction at these conditions was 97-99%.

The quantities of the materials prepared by the proposed method are sufficient for some practical uses, e.g., for saturating the melt in liquid-phase epitaxial growth. In other cases greater quantities are necessary. One of the possible ways to intensify the synthesis process is to increase the load weights. We have prepared in this way up to 0.1 mol of III-VI compounds (5). In the case of III-V's another approach may be more suitable - simultaneous synthesis in an number of ampoules mounted in a common furnace.

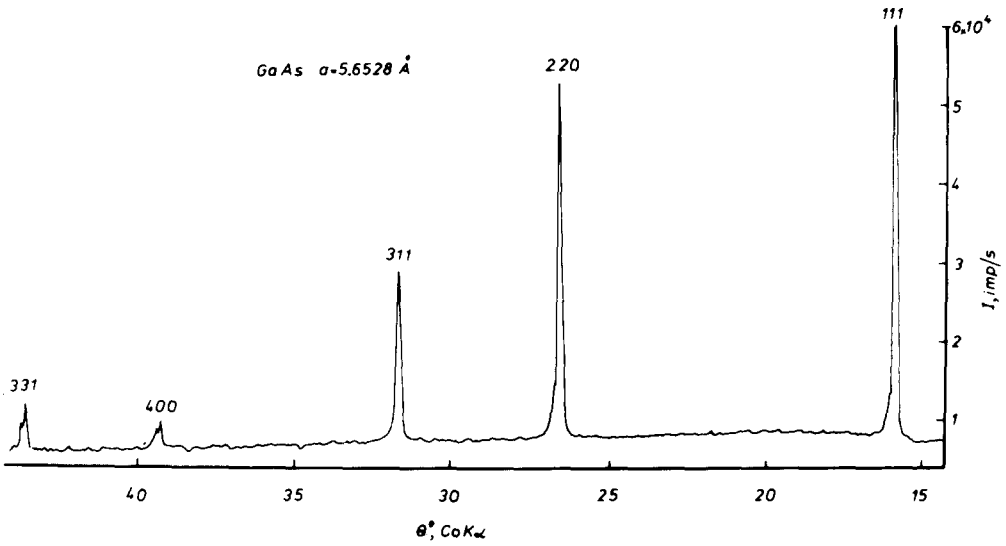


FIG. 1  
X-ray diffraction pattern of GaAs.

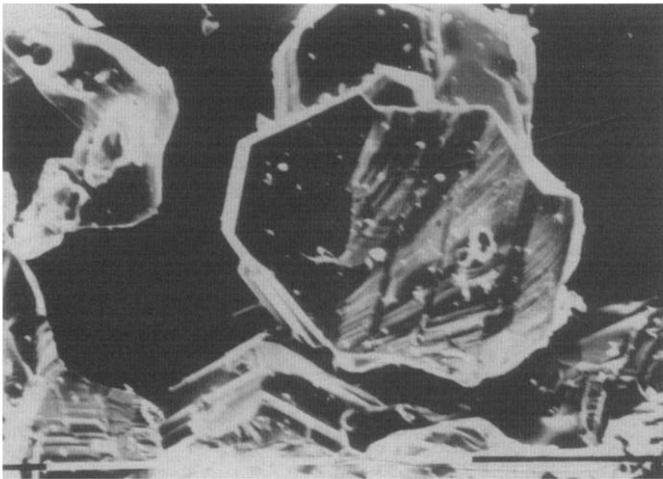


FIG. 2  
Scanning electron micrograph of GaAs. Marker length 100  $\mu\text{m}$ .

TABLE 1

Synthesis of Gallium and Indium Arsenides and Antimonides.

Initial mixture, quantity [mol]	Melting point of binary compound [°C]	Synthesis		Product, completeness of interaction [%]
		Temperature [°C] ±20°C	Duration [h]	
Ga + As 0.04	1237	580	140	GaAs 100
Ga + Sb 0.08	712	580	140	GaSb 100
In + As 0.03	942	580	150	InAs 100
In + Sb 0.05	536	500	70	InSb 100
In + Sb 0.07	536	400	110	InSb 100

Advantages and Applications of the Method

As can be seen from the above experimental results the synthesis is carried out at isothermal conditions at temperatures which are lower than, or comparable with, those of epitaxial growth. At these low temperatures:

- the elements in the ampoule are not contaminated during the synthesis, and the purity of the final product is determined mainly by that of the initial elements;
- no chemical interaction of, e.g., Al or Ga with the quartz ampoule takes place;
- the vapor pressures of the volatile elements are reduced, danger of ampoule explosion is eliminated and, hence, no complicated synthesis apparatus is needed;
- the vapor pressures of other gaseous species, such as Ga<sub>2</sub>O which hinders the synthesis of GaAs by the SSD method (1), are reduced; and
- the producing, measuring and controlling of these low temperatures is achieved by simple means: one-zone furnace, thermocouples, thermo-controllers of moderate accuracy.

The elements interaction is direct, hence:

- the produce is not contaminated by solvents,
- no elements or compounds are wasted as solvents, and
- the composition of the initial charge and that of the final product is controlled with high accuracy.

The total duration of heating is of importance for the completeness of the synthesis at a given temperature, hence the process may be interrupted and carried out again.

The relatively great process duration helps the product's homogenization.

The as-synthesized materials may be used for preparing bulk crystals and epitaxial layers, eutectic alloys, etc. The fact that the purity of the final product (the compound) corresponds to the purity of the initial components (the elements) explains the special interest in these materials for use in the low temperature crystallization methods, such as the travelling heater method (THM), the travelling solvent method (TSM), and as sources for epitaxial growth by vapor phase and liquid phase epitaxies (VPE, LPE). In this way, high purity single crystals and epitaxial layers without high temperature preparation steps in their "biography" may be grown.

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