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# VAPOUR PHASE GROWTH OF AlSb FROM THE CHLORIDES

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Polycrystalline and oriented AlSb films were grown on GaAs or GaSb substrates from chlorides in an alumina reactor designed to hold gaseous aluminium halides. The best epitaxial layers were obtained at 655°C on (111)GaSb, however they remain air sensitive.

## 1. Introduction

This work is part of a program developed to study AlSb as a material for photovoltaic conversion of solar energy. A recent publication [1] of experimental results discusses this topic and reviews published papers concerning this program.

Among several processes available for the synthesis of AlSb the vapour phase growth by chlorides had never been used to obtain AlSb, although this method has been successfully used to grow various III–V compounds, in particular AlP [2] and AlAs [3,4]. These may be compared in some aspects with aluminium antimonide.

## 2. Thermochemistry

Previous thermodynamic studies [5,6] of the different chemical equilibria involved in the Al–Sb–Cl–H system in the temperature range 650–1000°C give indication for the conception and choice of materials for crystal growth. For instance, the low equilibrium vapour pressure of elemental antimony has led to the use of separate Al and Sb sources, together with low hydrochloric acid concentrations, i.e. 0.5% in $H_2$. This feature has been pointed out by Jakowetz et al. [7] in the case of GaSb vapour phase growth. Antimony is transported mainly as $Sb_4$, and aluminium as a mixture of $AlCl_3$, $AlCl_2$ and AlCl, in proportions that are functions of the temperature.

## 3. Experimental

In this method volatile aluminium compounds (AlCl, $AlCl_2$ and $AlCl_3$) are produced by direct gaseous chemical reaction of HCl with liquid aluminium. The chlorides obtained are separately brought to the reaction chamber where they react with the group V hydride. In the case of antimony no stable hydride is available, thus aluminium chlorides react with a flow of antimony vapour ($Sb_4$).

The presence of very reactive compounds such as aluminium chlorides, melted aluminium, hydrochloric acid and hydrogen at high temperature implies severe selection of materials and special caution in planning the reactor.

The aluminium and the antimony sources are respectively held in two alumina tubes (16 mm OD) placed inside the main alumina tube (47 mm OD). An external silica tubing continuously swept by pure hydrogen prevents eventual leaks of tightness of alumina after temperature variations. The whole system is placed in a multi-zone furnace that ensures a suitable temperature distribution along the different parts of the reactor. The internal temperatures are measured by thermocouples introduced in a one-end closed alumina tube.

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The two compartments containing the source elements Al and Sb are connected in their cold part by PTFE tubing and at the other end are provided by graphite plugs bored by many holes to increase the gas velocity and thus the reaction.

In this way, any part in contact with aluminium chloride in the hot zone is alumina or graphite preventing any chemical reaction with the main reactor. In the same way all parts in contact with HCl (gas tubing, fittings, etc.) in the inlet part of the reactor are stainless steel. The whole aparatus is helium leak free.

The substrate holder is shaped from a piece of graphite and fixed at the closed end of an alumina tube where a thermocouple is introduced to measure the temperature very close to the substrate.

## 4. Experimental results

The layers of AlSb were studied using microscopy, X-ray diffraction and Laue photographs. The thickness was measured by optical methods.

On all the substrates used in the present study, growth of AlSb seems to be controlled by nucleation process. Crystalline islands appear on the substrate, the thickness and surface of which extend simultaneously. The coalescence of crystallites is only obtained when a critical thickness is obtained. For instance in the case of GaAs substrates at 780°C, on which a quick AlSb epitaxial growth occurs, the surface is not wholly covered by 20 μm high islands.

### *4.1. Polycrystalline substrates*

Polycrystalline deposits have been obtained on sintered alumina in the temperature range of 650–980°C. The most efficient conditions for a regular and good deposition are described in the table 1. The deposits are mainly composed of tetrahedral crystals, the dimensions of the largest depending on the temperature of the substrate. Identical results have been obtained on (0001) sapphire.

### *4.2. Single crystal substrates*

GaAs and GaSb have been used as substrates to obtain epitaxial deposits of AlSb.

### *4.3. Growth on GaAs substrates*

The lattice mismatch is large: $\Delta a/a = 8.5\%$, and without an accommodation film a high quality deposit cannot be expected.

As substrates, (100) and (111) oriented crystals have been used. With similar experimental conditions

Table 1
Experimental conditions of deposition of AlSb on different substrates

| Substrate | | Sources | | | | AlSb results, growth-rate |
|---|---|---|---|---|---|---|
| Nature | Temperature (°C) | Aluminium | | Antimony | | |
| | | Temp. (°C) | Flow (HCl 0.5%) (cm³/min) | Temp. [a] (°C) | Flow ($H_2$) (cm³/min) | |
| $Al_2O_3$ | 650–980 | 900 | 500 | 850 | 200 | Polycrystalline deposits, size of crystallites, $10 < l < 40$ μm/h |
| (100)GaAs (111)GaAs | 700–850 | – | – | – | – | Very rough oriented layers, 17 μm/h at 780°C |
| (111)GaSb | 650–683 | 948 | 400 | 900 | 120 | Oriented layers, 4 μm/h at 655°C |

[a] This temperature is not very significant, vapour flow mainly depends on the gaseous exchange above the antimony source.

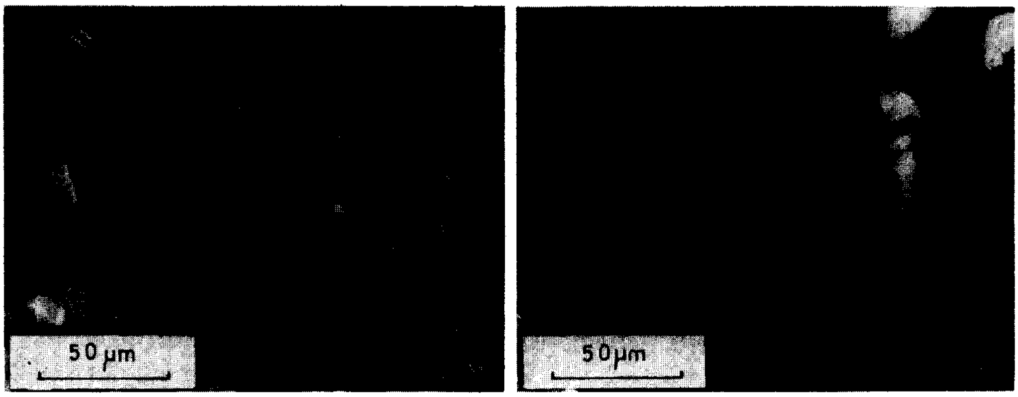


Fig. 1. Layers of AlSb on GaAs substrates: (a) (111)GaAs at 805°C; (b) (100)GaAs at 850°C.

of gaseous flow and temperature, the growth velocity is of the same order of magnitude whatever the substrate orientation. For example, 17 μm/h is measured on substrates at 780°C.

Every layer is built up with crystallites, the orientation and shape of which are characteristic of the orientation of the substrate, as shown on the photographs (fig. 1). X-ray photographs confirm the optical observations. The only reflexion peaks of AlSb are those of crystallographic planes parallel to the substrate.

With (111) substrates the B-face (non-metallic atoms) gives different results from the A one (metallic atoms). The layers seem smoother although even in this case the roughness of the surface is always visible.

In some X-ray photographs strong reflexion peaks of GaSb were observed. We assume that they are the result of substitution of surface As atoms by antimony. A liquid layer of GaSb at the growth temperature should, in this case, be an important element of the growth process. Although such lines are seen when a large excess of Sb occurs in the reactant gases, a more or less thin liquid layer probably acts in all cases in the nucleation process.

### *4.4. Growth on GaAs substrates*

AlSb and GaSb have very close unit cell parameters. The lattice parameter mismatch is only 0.65%. Despite its low melting point (710°C), GaSb is better substrate for AlSb epitaxy in the 650–680°C temperature range. With the experimental conditions of temperature and gaseous flow reported in table 1, (111) substrates have been used. The whole surface is covered and relatively smooth layers can be obtained as shown on photographs of surface and cleaved section (fig. 2).

The oriented nature of growth is confirmed by X-ray analyses (diffractometry and Laue photographs). The low melting point of GaSb allows only a relatively small range of temperatures. Below 650°C antimony vapours in excess in the gaseous flow condense. Although in our experimental conditions nothing else but AlSb deposit was observed in the reactor zone above 620°C, depositions have never been made at lower temperature to prevent condensation of antimony vapours in excess and formation of GaSb–Sb eutectic (590°C).

Besides, as already noted, the length of the formation zone of AlSb in the reactor decreased when the temperature decreased. AlSb is synthetized directly on the graphite ending of the tube containing aluminium, blocks it, and stops the chloride flow. Such behaviour has already been observed in the growth process of AlAs and mentioned by Ettenberg et al. [3] as a proof for non-equilibrium in the chemical reaction of the synthesis.

In all cases the layers of AlSb obtained on the different substrates mentioned are very moist-air sensitive. Kept in air, they gradually get darker, separate from the substrate and finally turn into

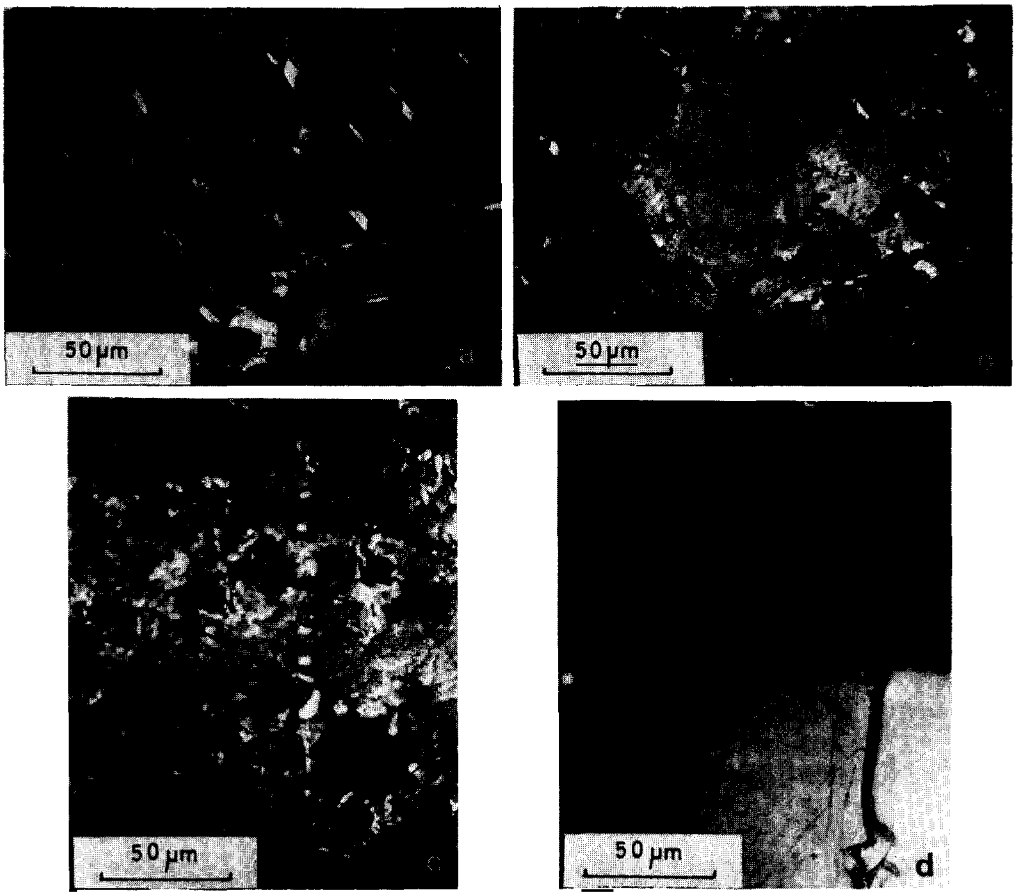


Fig. 2. Optical micrographs of oriented layers of AlSb on (111)GaSb substrates. (a), (b), (c) Different aspects of surface morphologies of layers obtained with experimental conditions reported in table 1. (d) Cleaved section of a 8 µm thick AlSb layer on (111)GaSb substrate.

powder in less than one day. To keep them for a longer time, they are protected in chloroform or trichlorethylene.

## 5. Conclusion

This work has shown the possibility of growing polycrystalline and oriented layers of AlSb from chlorides. GaSb is a suitable substrate for AlSb epitaxy although the experimental conditions required for its use are in a rather narrow range. A more convenient material is to be found as a substrate before epitaxial layers of AlSb are to be obtained by this method.

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