LETTERS TO THE EDITOR

Vapor-Phase Growth of Epitaxial $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ by the Open-Tube Method*

The techniques of chemical vapor deposition have been applied with great success to the epitaxial growth of gallium phosphide, indium phosphide, gallium arsenide, and their alloys. Vapor-phase epitaxial growth is the most important method of preparing single crystal films and multiple-layer epitaxial structure devices, since it is easy to grow high quality crystals and to vary, during growth, alloy compositions and the dopant concentrations in a well-controlled manner. The application of this technique, however, is restricted to compounds consisting of volatile elements such as phosphide and arsenides. In the case of antimonides, difficulties are raised by the low vapor pressure of antimony and their low melting points. It is likely that, for this reason, virtually no descriptions of the preparation of $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ by this technique have been presented. $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ is one of the materials that may provide highly improved Gunn devices.

In this paper, the experimental evidence that the chemical vapor deposition technique is useful for the preparation of epitaxial $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ is presented.

Epitaxial $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ ($0 \leq x \leq 0.2$) samples were grown in an open-tube flow system, as shown in Fig. 1. The reaction tube, which is made of fused quartz, has three branches. Two of the branches are the source zones and the other is the deposition zone. Each portion of this reaction tube is heated according to the temperature profile in Fig. 1, in a resistance furnace which has 10 heated zones regulated by SCR controllers. Commercial hydrogen chloride gas†, diluted with hydrogen gas to

Fig. 1 Schematic representation of apparatus for vapor-phase growth of epitaxial $\text{Ga}_{1-x}\text{In}_x\text{Sb}$.

2 mol%, is employed as a transport agent. The hydrogen gas employed as the carrier gas is purified by passage through a palladium-alloy diffuser. The dilute hydrogen chloride gas, combined in a given ratio with the hydrogen gas, is passed over the source materials and into the deposition zone.

The primary chemical reactions taking place in the source and deposition zones are suggested on the basis of the thermodynamical investigation of the chemical equilibrium of the $\text{Ga}_{1-x}\text{In}_x\text{Sb-HCl-H}_2$ system⁽¹⁾. At the source zones,

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† Purchased from Tsurumi Soda Co., the manufacture's reported purity is 99.99%.

and at the deposition zone,

where Ga, In, and Sb on the left side are derived from the source materials, i.e. the Ga-Sb alloy and In-Sb alloy, which are described below.

There is the difficulty in avoiding condensation of elementary antimony when introducing the antimony vapor into the deposition zone, since the antimony saturation vapor pressure is extremely low ($1-2 \times 10^{-1}$ Pa) in the deposition temperature range (455–470°C). Therefore it is required that the antimony vapor pressure in the source zone be controlled to be lower than the saturation vapor pressure of antimony in the deposition zone. In this work, 52 at%Ga-Sb alloy and 52 at%In-Sb alloy were employed as the source materials and were heated to 690 and 500°C, respectively, below the respective melting points of GaSb and InSb compounds. At these temperatures these materials exist in two phases, Ga (or In) liquid and GaSb (or InSb) solid, in thermal equilibrium. The presence of these two phases tends to minimize the vapor pressure of antimony in the dissociation pressure of GaSb (or InSb) at a given temperature. Furthermore, the GaSb (or InSb) source equilibrated with Ga (or In) liquid permits the composition of the gas phase components to be constant throughout the entire growth run, even though the composition of the source alloy changes as the run proceeds because of the difference in the transport rate between the source constituents.

GaSb substrates, 350 μm in thickness and having {111}B surfaces, were presented from single crystal† grown by a horizontal Bridgman method. After cutting, they were mechanically polished with a water suspension of alumina powder to a flat, mirror-smooth finish, chemically polished for 2 min in a mixture of hydrofluoric acid, nitric acid, and acetic acid in the ratio 1:9:20, rinsed with distilled water and

with methanol, mounted on a substrate holder and transferred to the growth apparatus.

In this way, $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ epitaxial layers with compositions ranging from 0 to 20 mol%InSb can be obtained. It should be noted that the deposition of $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ occurs selectively on the substrate only. As-grown surfaces of epitaxial layers were observed by a dark field microscope. An EPMA (electron probe microanalyzer) was used for the measurements of the compositions of the epitaxial layers. Layer thicknesses were determined from the composition change on line analyses of the cleaved section of the epitaxial layer.

Experiments on the effects of growth temperature and flow rate on the epitaxial layer are described below. Photograph 1(a)-(d) show surface morphology of $\text{Ga}_{0.9}\text{In}_{0.1}\text{Sb}$ epitaxial layers grown under identical conditions except for growth temperature. The layer grown at the low temperature of 436°C has a matte surface (Photo. 1(a)). Good epitaxial films are grown in a limited temperature range from 455 to 470°C. They have surface morphology of terrace-like microscopic structures (Photo. 1(b) and (c)), even though they appear to be mirror-like to the eye. Photograph 1(d) shows that a layer grown at 485°C exhibits tiny crystallites of condensed elementary antimony.

Typical growth parameters and results are listed in Table 1. The mole fraction of indium chloride in the vapor phase is always greater than that of indium in the grown layer. This indicates that there is a greater rate of incorporation of gallium than indium in the layer. The alloy composition of grown layers is nearly independent of the growth temperature, and is a function only of the composition of the vapor phase.

Electronic properties have not yet been examined.

The present study is only in the preliminary test stage of vapor-phase growth of $\text{Ga}_{1-x}\text{In}_x\text{Sb}$, although this is the first report on the epitaxial growth from the vapor phase. If future development and improvements are achieved, vapor-phase epitaxial growth techniques will be very useful for the practical preparation of $\text{Ga}_{1-x}\text{In}_x\text{Sb}$.

† Undoped P-type crystal with resistivity $7 \times 10^{-1} \Omega \cdot \text{m}$, purchased from Mining and Chemical Products Co., U.K.

Photo. 1 Surface morphology of $\text{Ga}_{0.9}\text{In}_{0.1}\text{Sb}$ grown at various temperatures: (a) at 436°C , (b) 455°C , (c) 470°C and (d) 485°C .

Table 1 Typical parameters and results on vapor-phase growth of epitaxial $\text{Ga}_{1-x}\text{In}_x\text{Sb}$.

Run No.	Source temp. ($^\circ\text{C}$)	Mole fraction of HCl	Flow rate of mixed gas (cc/min)	Growth time (h)	Substrate temp. ($^\circ\text{C}$)	Layer thickness (μm)	Composition (x)
45	Ga-Sb, 680	2×10^{-3}	100	5	470	17	0.10
	In-Sb, 500	2×10^{-3}	100		455	4	0.10
55	Ga-Sb, 690	6×10^{-4}	100	4	470	—	—
	In-Sb, 500	6×10^{-4}	100		455	10	0.08
56	Ga-Sb, 690	6×10^{-3}	105	4	470	7	0.10
	In-Sb, 500	6×10^{-3}	105		455	2	0.10
61*	Ga-Sb, 690	2×10^{-3}	100/55	2/2	470	—	—
	In-Sb, 500	2×10^{-3}	100/165		455	4	0.20

* In run No. 61, the mixed gas flows over the sources were both at the rate of 100 cc/min for 2 h, and for the following 2 h the flows were at the rates of 55 and 165 cc/min over the Ga-Sb source and the In-Sb source, respectively.

REFERENCE

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