NEW SEMICONDUCTORS AND THEIR POSSIBLE APPLICATIONS*)

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Using GasSb substrates, epitaxial layers of $Al_xGa_yIn_{1-x-y}Sb$ and bulk $GaP_xAs_ySb_{1-x-y}$ crystals were investigated. In these alloys three different atoms share a single sublattice in the sphalerite structure. The similar cationic pseudoternaries (AlGaInP or AlGaInAs) cannot be grown by LPE because of large Al segregation. The anionic types (InPAsSb, GaPAsSb) can be prepared by LPE, but miscibility gaps and strong segregation of P make difficulties.

Our AlGaInSb samples have been prepared by the LPE method giving homogeneous in composition p- and n-type layers and p-n junctions, as well. GaPAsSb was prepared as bulk single crystals using transport reactions. Preliminary measurements show that the cationic $Al_xGa_yIn_{1-x-y}Sb$ pseudoternary with a composition of $x = 0{\cdot}97$, $y = 0{\cdot}02$ can be applied to developing detectors. These junction-type devices function efficiently in the spectral regions where the Ge photodiodes work. The other, anionic pseudoternary $GaP_xAs_ySb_{1-x-y}$ has shown brilliant photo- and cathodoluminescence. The composition of the measured phase was $x = 0{\cdot}36$ and $y = 0{\cdot}62$. Lattice constant and composition measurements showed that while the cationic alloy composition falls into the indirect band gap region, the anionic luminescent phase is a direct material. This gives a possibility of developing light sources in the visible range.

1. INTRODUCTION

The continuously growing field of microwave and optoelectronic applications increases rapidly the demand on new semiconductors with particular properties. Optoelectronics requires laser, LED and detector materials in a wide optical range between $0{\cdot}5-10.0\ \mu m$. In these materials the recombination properties have to be chosen according to the requirements. The elementary semiconductors being indirect materials generally do not suit these purposes, and similarly, the charge carrier mobility of Ge and Si is low for high frequency applications; thus the microwave semiconductor devices also need compound semiconductors.

In semiconductor devices, particularly in optoelectronic structures, all of us rely on obtaining long minority carrier life-time (τ) an diffusion length (L). Among the important practical applications there are many heterojunction structures. Since interfacial defects (mismatch, misfit network etc.) usually reduce the τ and L par-

*) Invited talk at the International Conference on Radiative Recombination and Related Phenomena in III–V Compound Semiconductors, Prague, 4–7 October, 1983.

ameters in a device, it is very important to obtain good matching between the materials used. The growth of materials with a given bandgap (E_g) that is optimized for a particular application and the achievement of the precise controll of lattice parameter a_0 which matches the substrate are difficult. These difficulties can be circumvented by applying quaternary semiconductors. In a quaternary system there are four degrees of freedom, therefore, a wide range of compositions (as well as E_g) belongs to a definite lattice parameter value a_0, and vice versa. This is the reason why recently the interest in quaternary $A^{III}B^{V}$ alloys has arisen considerably. Among the possible compounds only the GaInAsP has thoroughly been examined as a laser material. No detailed study of pseudo-ternary $A^{III}B^{III}C^{III}D^{V}$ or $A^{III}B^{V}C^{V}D^{V}$ compounds has been performed. In these systems one of the sublattices consist of three, different ions. AlGaInSb [1–3], GaPAsSb [4, 5] and InPAsSb [6] are the experimentally known quaternaries of this kind. In this paper the preparation and the possible applications of Al_xGa_y . . $In_{1-x-y}Sb$ and $GaP_xAs_ySb_{1-x-y}$ are investigated.

2. EXPERIMENTAL

2.1. Preparation of pseudo-ternary antimonides

In semiconductor technology both single crystals and epitaxial layers are used. Single crystals are employed as starting material or as a substrate on which a particular epitaxial layer structure can be built. Generally, quaternaries are known in the form of epitaxial layers, because homogeneous bulk quaternary crystals can hardly be prepared. The GaPAsSb has also been known as an epitaxial intermediate layer between a GaAs and GaAsSb layer [4]. No previous work on the preparation of homogeneous, bulk crystalline phase has been published. Recently, we have succeeded in preparing this phase using a transport process [5]. The initial charges (GaP, GaAs and GaSb) were introduced into a quartz ampoule and the components were dissolved in GaSb molten phase at a temperature of 800 °C. After homogenization, the temperature was raised up to 1100 °C. Lowering the ampoule in a negative temperature gradient, single crystals of GaPAsSb were grown in the ampoule tip and on the surface of the solidified melt.

The existence of AlGaInSb was proved in bulk phase [1], but no epitaxial layer was prepared previously. Using In-rich melts and (111) GaSb substrates we have prepared homogeneous epitaxial layers using horizontal LPE methods [2, 3]. The cooling rate was ~1 °C min^{-1}, and a supercooling of 5–20 °C was applied. A double substrate system was used. Over the first wafer the melt saturation was completed, while the LPE growth of AlGaInSb was performed onto the second substrate. Prior to growth the supercooling value (ΔT) was set in, then the solution was brought into contact with the growth substrate. Using a constant cooling rate, 1–10 μm thick epitaxial layer was grown, cooling the melt over the substrate for a while.

2.2. Investigation of quaternary antimonides

The solid composition of single crystals and epitaxial layers was measured with a JEOL JSM 35 type microprobe analyzer using both wavelength and energy dispersive analysis. The perfection of epitaxial layers was investigated using X-ray rocking curves. Lattice constants were measured by X-ray diffraction. The cathodoluminescence of the samples was observed under the electron beam of SEM during the topological study of the sample surfaces. Exciting the semiconductors at 4 K by Ar-ion laser, the photoluminescence of the quaternaries was also detected. The measured composition data were processed by digital data processing. Standard and background data were collected in an MCA data memory of an ORTEC 6230 system. The X-ray measurements were performed using CuK_α radiation and (222) reflexions.

For analyzing the growth rate dependence on orientation, polycrystalline GaSb substrates grown by a modified Bridgman method [7–9] were used on which both the substrates grain orientation and the orientation of the overgrown AlGaInSb epitaxial layers were determined [10].

3. RESULTS

3.1. $GaP_xAs_ySb_{1-x-y}$ system

The pseudo-ternary GaPAsSb was known as an intermediate layer between GaAs and GaAsSb. This buffer is used to eliminate the lattice mismatch between the binary and ternary material. Owing to the strong segregation coefficient of P, first a lattice matching quaternary layer is formed on the GaAs surface, then the composition changes continuously down to the GaAsSb composition because of the depletion of P in the melt. Neither the detailed study of this semiconductor nor the preparation of the homogeneous $GaP_xAs_ySb_{1-x-y}$ phase have been described. Recently, we have succeeded in producing bulk, homogeneous solid phase of this compound [5]. A characteristic crystal can be seen in fig. 1 (see plate III, p. 494d). The individual crystals were analysed and the composition was found to be $x = 0{\cdot}366$ and $y = 0{\cdot}619$. During SEM investigation the phase showed a brilliant, red luminescence. Exciting the semiconductor at 4 K by Ar-ion laser, bright, red photoluminescence was also observed. A characteristic energy distribution is presented in fig. 2. This indicates that this pseudo-ternary GaPAsSb offers possibility of developing light sources. The triangular composition diagram of the system (fig. 3) shows that the direct band gap region covers a remarkable part of the composition field. In order to get a suitable, homogeneous composition, extended work has to be done. The optimized design of p-n junction, however, is an extremely complex subject because of the segregation of P. The lattice matching, in principle, can be achieved for both GaAs and InP, as it can be seen in fig. 4, where E_g vs. a_0 function is drawn. InP is suited to GaPAsSb compositions falling into the direct band gap region, while both direct and indirect band gap

GaPAsSb quaternaries can be lattice matched to GaAs. This means that good-quality substrate materials for a perspective development are available, but phase relations and segregation effects have to be determined for further technological progress.

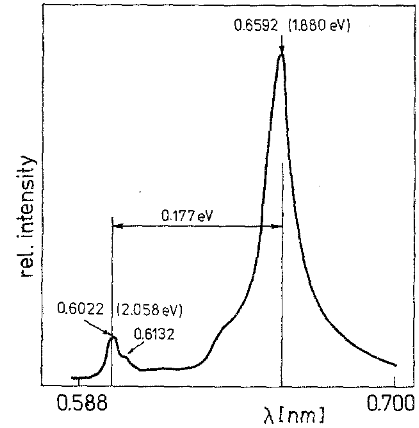

Fig. 2. Photoluminescence of $GaP_xAs_ySb_{1-x-y}$ single crystal excited at 4·4 K by an Ar-ion laser.

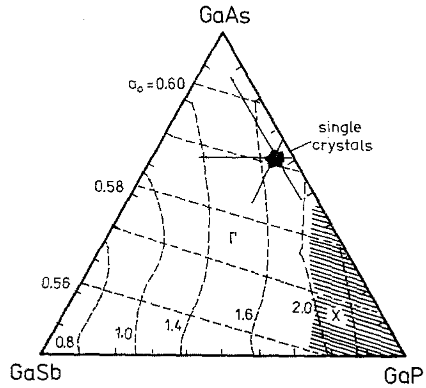

Fig. 3. Triangular composition diagram of pseudoternary GaPAsSb. The star denotes the composition field of the single crystal growth.

3.2. $Al_xGa_yIn_{1-x-y}Sb$ system

Using GaSb substrates, quaternary III–V compounds of the $A_x^{III}B_y^{III}C_{1-x-y}^{III}Sb^V$ type have also been investigated. These compounds are also very interesting because three different cations share a single sublattice. The relating cationic pseudo-ternaries (AlGaInP or AlGaInAs) cannot be grown by LPE because of the large Al distribution

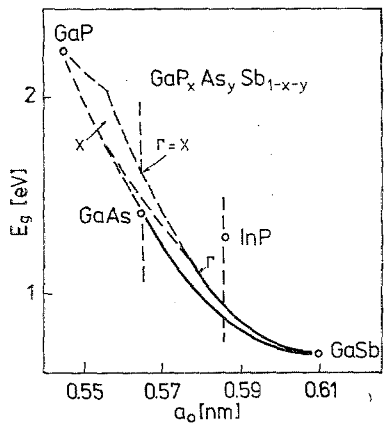

Fig. 4. Band gap vs. lattice constant curves for $GaP_xAs_ySb_{1-x-y}$. Dashed lines denote the indirect band gap region. The position of X and band minima are also presented.

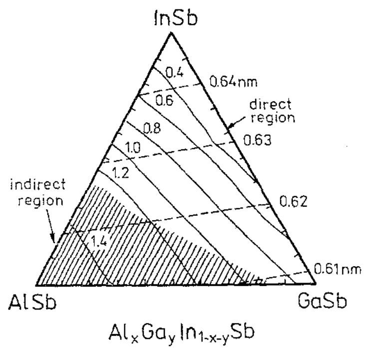

Fig. 5. Triangular composition diagram of $Al_xGa_yIn_{1-x-y}Sb$. The shaded area covers the indirect band gap region.

coefficient. In our laboratories AlGaInSb have been prepared by LPE [2, 3]. No previous work has been published on the LPE growth of this material. In contrast with the corresponding phosphide and arsenide, this material is grown from quaternary melts applying strong (5 – 20 °C) supercooling, although in this system strong Al segregation can also be observed. Owing to this fact the composition of the formed solid is at the AlSb corner of the phase diagram as it is seen in fig. 5. The solid composition measured by microprobe analysis in epitaxial $Al_xGa_yIn_{1-x-y}Sb$ was

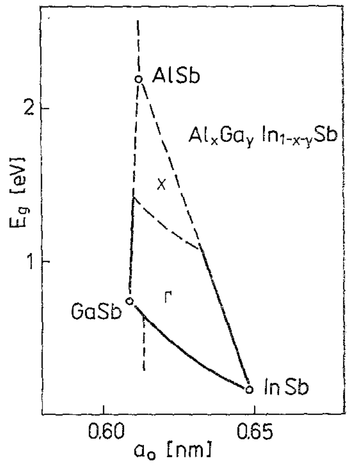

Fig. 6. The lattice constant dependence of the band gap (E_g) values in the $Al_xGa_yIn_{1-x-y}Sb$ system. The dashed lines limit the indirect band gap regions.

found to be $x = 0{\cdot}972$ and $y = 0{\cdot}014$. X-ray rocking curves show that the epitaxial layers give diffraction as narrow as the substrate itself. From the peak separation the lattice parameters of the grown layers have been determined [11] and were found in the region of $0{\cdot}6136\ nm < a_0 < 0{\cdot}6141\ nm$. The half-with of the reflections in the rocking curves was less than 0·10° showing the perfection of thin (<1 μm) and thick (>1 μm) epitaxial layers. The lattice mismatch is not too large, it has a value of 0·7 to 0·890%. (a_0 value of GaSb is 0·60970 nm.) Unfortunately this mismatch cannot be diminished, because the quaternary can be lattice matched only to AlSb as seen in fig. 6, where the E_g vs. a_0 curve is shown. To study the dependence of growth rate on substrate orientation, polycrystalline GaSb substrates were also used for LPE. On differently oriented grains the different growth rates have been determined. Using the same experimental conditions in cases of mono- and polycrystalline substrates, a very strong growth anisotropy was found. A definite inhibition of growth in particular orientations has been observed. On twinned regions, on the one side, thick epitaxial overgrowth was formed, however, on the other side, no epitaxial layer was grown. A characteristic view of a part of such overgrown polycrystalline GaSb substrate is presented in fig. 7 (see plate III, p. 494e). Revealing the grain structure by correspondence was found between the polycrystalline structure and the epitaxial topology. In principle, owing to its physical parameters this material could substitute Ge in IR detectors, therefore, the production of good-quality epitaxial structures is important. Successful growth of layers and p-n junctions can be achieved only at high supercooling ($\Delta T > 5$ °C) when at the very moment of the melt-solid contact a rapid formation of the quaternary solid on the substrate surface takes place. Doping the melt with Te, p-AlGaInSb/n-AlGaInSb p-n junctions were also grown. For growing p-layer of AlGaInSb, no dopant was added into the melt because Sb vacancies make p-type layers. Applying ring Au contact to the quaternary surface, a simple photodiode structure was developed. (The back contact was AuGe eutectic.) The diode chip is shown in fig. 8 (see plate III, p. 494f). Preliminary measurements show that these AlGaInSb junction devices function efficiently in those spectral ranges where the Ge photodiodes work, the laboratory samples peak response is at about 1·4–1·5 μm. It is well known that the presently applied Ge IR detectors in the optical telecommunication are too noisy, therefore a new detector with a lower noise level at room temperature would be superior to them. It is important to stress that this quaternary material promises new detector material instead of Ge, and in principle a necessary development, the Ge diodes could be replaced by AlGaInSb photodiodes or avalanche photodiodes. Performance of such devices is the aim of our future efforts.

Received 4. 10. 1983.

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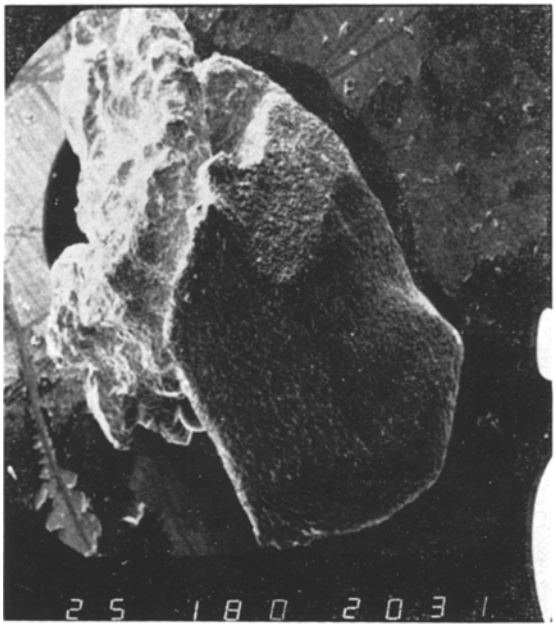
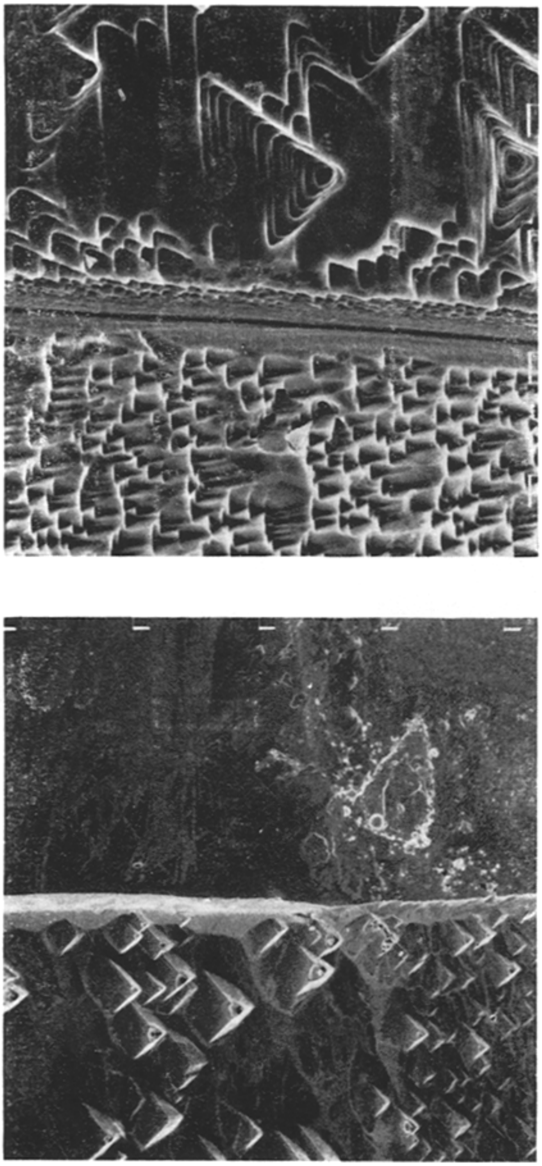


Fig. 1. Characteristic $GaP_xAs_ySb_{1-x-y}$ crystal grown by transport in a closed quartz ampoule.



a)

b)

Fig. 7. Growth rate dependence on orientation. Epitaxial overgrowth on two, differently oriented grains. (a) Chemically revealed structure on GaSb substrate back side. (b) Epitaxial AlGaInSb layer grown onto the above grains.

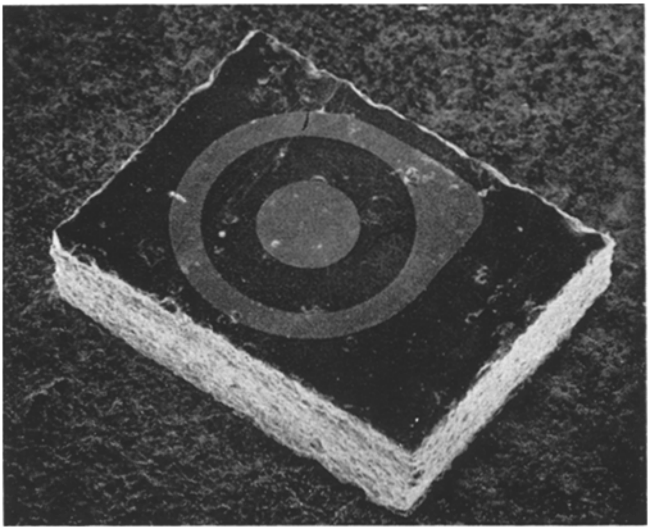


Fig. 8. Heteroepitaxial p-GaSb/p-AlGaInSb/n-AlGaInSb photodiode structure.