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ELECTROEPITAXIAL GROWTH OF GaSb AND AlGaSb THICK EPITAXIAL LAYERS*

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Semi-bulk epitaxial layers of GaSb and AlGaSb up to 3 and 1 mm thick, respectively, were successfully grown by the liquid phase electroepitaxy on GaSb substrates. The growth procedure allowed us to achieve high crystallographic perfection as well as compositional uniformity of ternary layers.

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1. Introduction

The ternary alloy $Al_xGa_{1-x}Sb$ offers a wide range of applications in modern electronics. For example, it is a prospective material for optoelectronic devices in the near infrared region (0.81 to 1.69 μm). Especially, $Al_{0.13}Ga_{0.87}Sb$ is an attractive material for avalanche photodiodes in the wavelength range used in optical communication (1.5 μm). Moreover, $Al_{0.22}Ga_{0.78}Sb$ may be used as a lattice matched substrate for ZnTe provided a high quality ternary material in a bulk form suitable for cutting it into wafers is available. The aim of this paper is to report our first results of bulk AlGaSb ternary alloys growth with a use of the liquid phase electroepitaxy (LPEE). As shown previously, LPEE, due to the constant growth temperature and the presence of electromigration, enables to grow semi-bulk multicomponent crystals with a very high compositional uniformity. The details of the LPEE technique as well as a discussion of composition stabilization is presented elsewhere [1].

2. Growth procedure

The first step in the growth procedure is preparation of AlGaSb polycrystalline source material of a required composition. This is achieved by loading of alloy constituents Al, Ga and Sb into the graphite container placed in the evacuated and sealed quartz ampoule. The melt constituents are loaded into the ampoule in

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the stream of high purity nitrogen, otherwise, Al reacts easily with oxygen which changes the composition of the ingot. Finally, the ampoule is heated 2 hours at the temperature by 50–100°C higher than the liquidus temperature of the melt. This procedure is followed by a quenching process in liquid nitrogen. The source materials with compositions up to $x = 0.4$ were produced by this technique.

The LPEE growth is performed at 535°C in a horizontal reactor system. The polycrystalline AlGaSb source material is placed on the top of the melt in order to supply the solutes to the solution and compensate its depletion during the epitaxial growth. The composition of the ternary melt is adjusted to the composition of the source material (and thus, to the composition of the layer to be grown) according to the Al–Ga–Sb phase diagram [2]. After 8 hours of the system homogenization an electrical contact to the substrate back surface is prepared at the growth temperature by squeezing the Ga(90%wt)Al(10%wt) solution under the substrate wafer. Then, the positively biased GaSb substrate is slid under the solution and the electric current with a density of 5–10 A/cm^2 is passed through the solid–liquid interface. The electric current starts and sustains crystallization of the epilayer. The growth is stopped after 70–150 hours by switching off the electric current and cooling down the whole system.

3. Results and discussion

The scanning electron microprobe (SEM) analysis of polycrystalline AlGaSb source materials shows the large, microscopic fluctuations of their compositions. The ingots contain high density of AlSb-rich crystallites in GaSb-rich matrix, which is a result of a fast Al segregation during the first instants of the melt quenching. The bulk composition of the source material is determined by cutting out $3 \times 4 \times 2$ mm^3 samples from different places of the ingot along its length. Then, the samples are dissolved in the aqua regia and amounts of Al, Ga and Sb are measured by atomic emission spectroscopy technique. This analysis reveals high uniformity of macroscopic distribution of elements and good crystal stoichiometry. The obtained compositions are very close to those calculated from concentrations of elements loaded. Moreover, no traces of the aluminium oxide are detected. This proves the correctness of the applied procedure of source material preparation.

An important step in the LPEE growth is preparation of the electric contact to the substrate back surface. A quality of this contact determines lateral uniformity of electric current flow through the solid–liquid interface, which in turn affects the quality of the epitaxial layer (e.g. thickness uniformity). Usually, the electric contact is prepared by introducing of a small amount of undersaturated melt under the substrate wafer. This leads to a partial dissolution of the substrate back surface and low resistivity of the contact. Bischopink and Benz [3] have reported a use of a layer structure of liquid Ga/Ta foil/In–Ga solution as the electrical contact between the GaSb substrate and the graphite anode. The contact was prepared at room temperature and outside the growth reactor. Thus, the contact nonuniformity was highly probable due to a possible oxidation of the contact solution and/or GaSb surface. This might be the reason that a use of as thick as 5 mm GaSb substrate was necessary to obtain laterally homogeneous electric current flow and to

grow high quality epitaxial layers. In our case, the electrical contact to the substrate is prepared at the growth temperature after long pre-baking of the contact melt and the substrate in a stream of high purity hydrogen. Additionally, a high concentration of Al in the contact melt seriously reduces the dissolution of GaSb. Thus, only thin ($\approx$ 120 μm), and uniform in thickness, layer of GaSb substrate is dissolved by the contact liquid. Therefore, a use of 400 μm thick substrates is sufficient for the successful growth of electroepitaxial layers on GaSb.

We have noticed a strong influence of the sign of the Peltier effect at the solid–liquid interface on the quality of the substrate–epilayer phase boundary. For the *n*-type GaSb (Te doped) substrates the solid–liquid interface is cooled due to the Peltier effect [1]. Thus, both the temperature gradient induced in the solution by Peltier effect as well as electromigration transport the solutes towards the substrate. This results in the high quality interface between the substrate and the growing epilayer. For the *p*-type (undoped) GaSb substrates, however, the sign of the Peltier effect is reversed and a competition between the solutes transport by electromigration and diffusion in the Peltier effect induced temperature gradient takes place. It can be shown [1] that the Peltier effect governs the growth/dissolution phenomenon at the beginning of the process, i.e. when the electric current is turned on. Then, the solution in a vicinity of the substrate becomes undersaturated which leads to a local dissolution of the substrate and to a substrate–epilayer phase boundary roughness. We avoid this undesirable effect by a slow (instead of ramp) increase in the electric current to its final value. This process is combined with an initial supersaturation of the growth solution. In order to optimise this procedure and observe the growth/dissolution processes at the beginning of the layer deposition we use an in situ growth monitoring technique [4, 5]. This allowed us to protect a planarity of the substrate and to obtain high quality substrate–epilayer interface even for *p*-type substrates.

Thick epitaxial layers of GaSb with thicknesses up to 3 mm and $Al_xGa_{1-x}Sb$ ($x < 0.4$) with thicknesses up to 1 mm were grown on the (100) GaSb substrates. The SEM examination of the ternary layers revealed their high compositional uni-

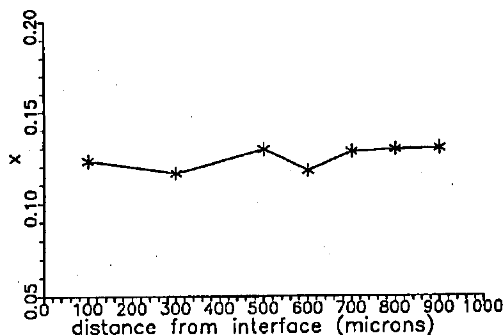

Fig. 1. Aluminium concentration vs. thickness of 1 mm thick $Al_xGa_{1-x}Sb$ ($x = 0.13$) epilayer grown by LPEE technique.

TABLE

Electrical parameters of GaSb and AlGaSb layers at room temperature.

Sample	Free carriers	
	concentration [cm^{-3}]	mobility [$cm^2/(V\ s)$]
GaSb undoped	$p = 1 \times 10^{17}$	500
GaSb:Te	$n = 3 \times 10^{17}$	2990
GaSb:S	$p = 4 \times 10^{16}$	300
AlGaSb:Te, $x = 0.18$	$n = 2 \times 10^{18}$	156
AlGaSb:S, $x = 0.21$	$p = 2 \times 10^{16}$	100

formity along the entire thickness. As an example, the SEM composition profile taken along the growth direction of 1 mm thick $Al_{0.13}Ga_{0.87}Sb$ layer is shown in Fig. 1. The layers were doped with Te or S. Room temperature values of free carriers concentration and mobility as measured by the Hall effect are presented in Table. Before the electrical characterization the substrates were removed by mechanical polishing. Undoped layers showed p-type conductivity which is commonly attributed to the high concentration of antimony vacancies in GaSb-based materials. n-type conductivity of the layers was obtained by Te doping. However, due to a high segregation coefficient of tellurium at the growth temperature the precise control of the doping level was difficult if the elemental Te was loaded to the melt. Incorporation of sulphur to the layers during their LPEE growth was studied. Introduction of Sb_2S_3 to the solution was found to be a convenient way of doping with S [6]. As seen from Table this leads to the partial compensation of native acceptors in the layers.

Concluding, we report here a successful growth of semi-bulk layers of AlGaSb of a high compositional uniformity. We report also first results of n-type doping of GaSb and AlGaSb.

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