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# Kinetics and edge-growth effects of GaAs LPE layers grown in the Ga–As–Bi system

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Studies of the growth kinetics of GaAs epitaxial layers obtained from Ga–As and Ga–As–Bi solutions are compared in this work. We applied an equilibrium cooling method in a classic liquid phase epitaxy (LPE) system with the use of slider-type boats. The studies were carried out for Ga–As–Bi solutions containing 0 to 95% wt% Bi and also for Ga–As solutions at the same technological parameters of the growth process for comparison purposes. It is shown that in the applied range of bismuth concentration in the alloys, the GaAs growth rate is 0.5 to 3 times higher than for classic Ga–As solutions. It is found that the presence of bismuth in the solutions eliminates a disadvantageous GaAs edge-growth on the layer edges and considerably decreases the number of meniscus lines on the deposited layer surface.

## 1. Introduction

The application of bismuth as a solvent (instead of the commonly used gallium) in the process of GaAs LPE results in a lowering of carrier concentration and a considerable increase of its mobility in the deposited GaAs layers [1, 2]. The effect is explained by a high coefficient of bismuth and silicon interaction $-\alpha_{Si-Bi}$ in solutions [1]. It is known that silicon is a residual dopant, which is always present in GaAs deposited by the LPE technique.

As in the deposition of GaAs from a bismuth solution we have to deal, in fact, with a Ga–As–Bi three-component system, and the obtained material has better electrophysical properties, it is useful to study the growth kinetics of GaAs epitaxial layers from Ga–As–Bi solution in a wide range of bismuth concentration in the applied solutions.

The phase diagram of the Ga–As–Bi system in the range of Ga–Bi–GaAs has been experimentally defined in previous work [3]. It is also known that the GaAs compound is the only interphase of a constant composition in the analysed system; its segregation coefficient and solubility with respect to GaAs are very low [1–3, 5].

## 2. Experimental procedure

The deposition of GaAs epitaxial layers was carried out in a horizontal open reactor with the application of an equilibrium cooling technique (non-stationary LPE system) [6] and with the use of a typical slider-type graphite boat. Hydrogen purified by means of a palladium purifier was used as a working atmosphere. The solvents were saturated with arsenic at the starting temperature of deposition for 2 h, using dummy GaAs substrates for the purpose with identical parameters to the real substrates. Next, by moving the slider, the alloy saturated with arsenic was brought into contact with the real substrate, and a programme of linear cooling was initiated with a rate $V_T = 0.25\,\mathrm{K\,min^{-1}}$. The deposition time of the layers was $t = 30\,\mathrm{min}$. The process was repeated for eight compositions of the initial solution and for two starting temperatures of deposition, $T_{p_1} = 1073\,\mathrm{K}$ and $T_{p_2} = 1113\,\mathrm{K}$. The mass of the initial solutions ($m_{Ga} + m_{Bi}$) was constant and equal to 2 g, which for the utilized channel of the solution container with a capacity of $0.626\,\mathrm{cm^2}$ resulted in the height of the liquid phase column varying from 3.2 for 0 at % Ga to 5.1 mm for 100 at % Ga, depending on the composition (see Fig. 1). If the arsenic diffusion coefficient is assumed to be $D^l_{As} = 4$ to $8 \times 10^{-5}\,\mathrm{cm^2\,sec^{-1}}$ [7], and assuming an infinite source diffusion model (i.e. constant concentration on the liquid–solid phase boundary), the relaxation time is greater than the growth time. GaAs:Cr (100) substrates produced by Institute of Electronic Materials Technology CEMI with $\varrho > 10^7\,\Omega\,\mathrm{cm}$ and a dislocation density less than $5 \times 10^4\,\mathrm{cm^{-2}}$ were used. The substrates were cut to dimensions of 10 mm × 11.5 mm, cleaned before the process in organic solvents and then surface etched in a standard $H_2SO_4:H_2O_2:H_2O$ solution such as 12:1:1 volume ratio. The bismuth and gallium used were of 6N purity.

## 3. Results and discussion

### 3.1. Thickness and average rate of layer growth

Thicknesses of the obtained layers were measured by means of an interferometer microscope. Profilograms of the layers were also taken, and in the case when gallium was a solvent the mass increment was averaged to give the value per surface layer. The relations of thickness and average growth rate of the obtained layers for the two chosen temperatures against the input solution composition are shown in Figs 2 and 3, respectively.

Within the range 85 to 96 at % Ga a sharp increase of GaAs thickness and growth rate is noticeable (up to

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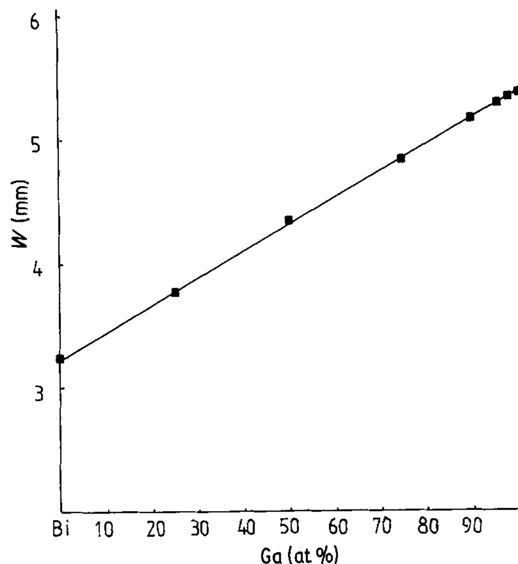


*Figure 1* Dependence of thickness of initial solvent on its composition at a temperature of 1073 K.

three times with respect to the classic Ga–As system) (Fig. 4). As is known according to a diffusive model of epitaxial growth from a liquid phase with semifinite thickness [7], both the layer thickness and growth rate for a defined process time depend mainly on the value of the liquidus line slope and the arsenic diffusion coefficient in the liquid phase. When we consider the slope of the liquidus line $\partial T/\partial C^{1}_{As}$ for the Ga–As–Bi phase diagram given by Evgenev and Ganina [3] (liquidus isotherms were given there for slightly higher temperatures than we have applied), no other than monotonic changes of the parameter are observed in this range of the solution system. So, it should be concluded that the arsenic diffusion coefficient in Ga–As–Bi solutions is responsible for the character of the obtained growth lines. According to our opinion, the parameter changes (depending on the solution concentration) can be caused by the following factors:

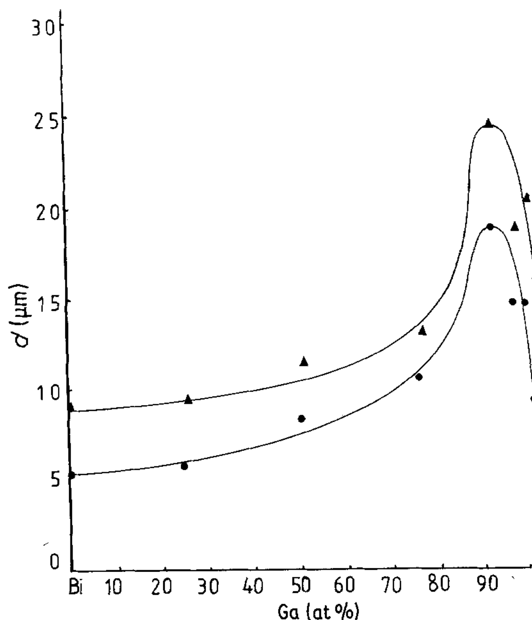


*Figure 2* Thickness $d$ of GaAs epitaxial layers against the composition of $Ga^{L} + Bi^{L}$ initial solvent for two starting temperatures of layer growth, (●) $T_{p_1} = 1073\,K$ and (▲) $T_{p_2} = 1113\,K$; $V_T = 0.25\,K\,min^{-1}$ and $t = 30\,min$.

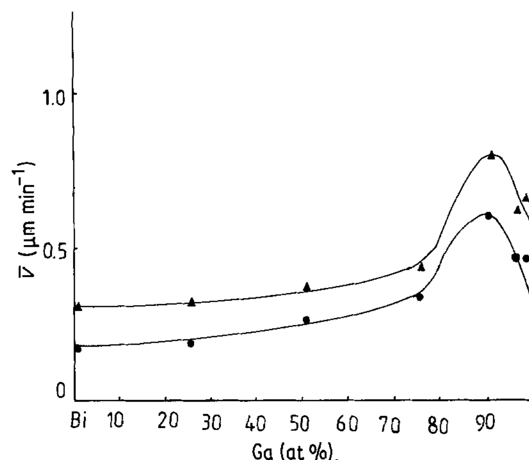


*Figure 3* Average growth rate of GaAs layers against the composition of $Ga^{L} + Bi^{L}$ initial solvent for two starting temperatures of layer deposition, (●) $T_{p_1} = 1073\,K$ and (△) $T_{p_2} = 1113\,K$; $V_T = 0.25\,K\,min^{-1}$ and $t = 30\,min$.

1. The existence of a limited solubility area in the liquid phase of the Ga–Bi system [3], and thus a more complicated mechanism of the diffusion itself.
2. A different tendency of the solutions to supercool, with the possibility of crystallization in the bulk of the solution (two-phase LPE).
3. An edge-growth of GaAs on the layer edges for a gallium concentration in the solution of more than 96 at %.

However, as the thickness of the GaAs layer obtained from a gallium solution agrees well with the values obtained by Crossley and Small [8], and as the solutions based on gallium withstand supercooling by $\Delta T \approx 20\,K$, the first factor above should be found the most important. An exact explanation of the growth kinetics of GaAs layers from Ga–As–Bi solutions requires further studies with a consideration of all the above-mentioned factors.

## 3.2. Edge-growth of layers

During the deposition of $A^{III}B^{V}$ compounds by the LPE method, and also of their solution in the solid

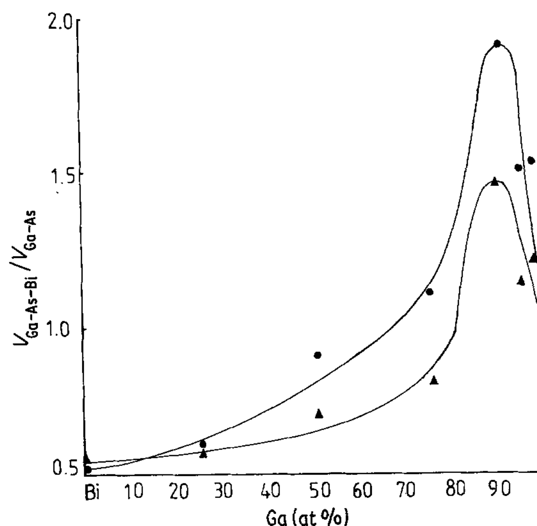


*Figure 4* Ratio of GaAS layer growth rate obtained from a Ga–As–Bi solution, to GaAs layer growth rate obtained from a Ga–As solution. (●) $T_{p_1} = 1073\,K$, (△) $T_{p_2} = 1113\,K$; $V_T = 0.25\,K\,min^{-1}$ and $t = 30\,min$.

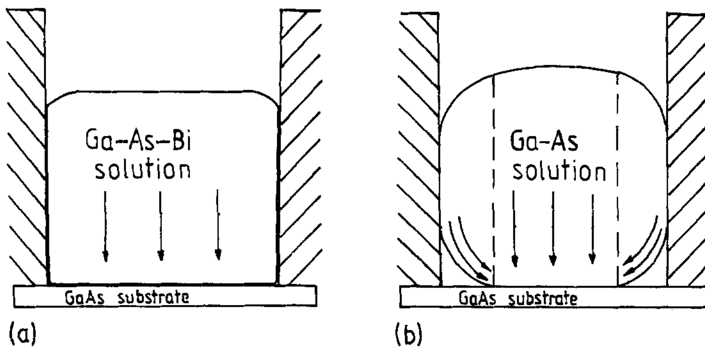


*Figure 5* Diagram presenting the mechanism of (a) one- and (b) two-dimensional arsenic diffusion in Ga–As–Bi and Ga–As solutions, respectively. For (a), $\partial^2 C^l_{As}/\partial x^2 = (1/D^l_{As})(\partial C^l_{As}/\partial t)$; for (b), $\partial^2 C^l_{As}/\partial x^2 + \partial^2 C^l_{As}/\partial y^2 = (1/D^l_{As})(\partial C^l_{As}/\partial t)$.

phase, a disadvantageous phenomenon of layered edge-growth commonly occurs. In general, it consists in that the thickness of a deposited layer near the edges of a substrate is thicker than on the remaining surface. In certain cases the edge-thickness of the epitaxial layer can be several times higher than the uniform layer thickness. There are several theories of this edge-growth. They have been compiled by Astels *et al.* [9]. In our opinion, the convection theory and the double-diffusion theory are the most probable of them.

According to the first of these, excessive edge-growth is explained by an influence of convection streams in the liquid phase near the walls of the alloy chamber, caused mainly by a temperature difference between the boat wall and the bulk of solution. So, an additional transport of semiconductor component (apart from diffusion) occurs towards the surface of the solid phase. The second theory, shown schematically in Figs 5a and b, assumes an additional stream parallel to the substrate surface (the $Y$ direction), apart from the basic diffusion stream along the $X$-direction. The occurrence of the additional diffusion stream is related to the wetting angle (as in the Ga–GaAs case) causes the formation of a gas-phase area at a certain point (Fig. 5b), which is a condition of the additional diffusion component to occur. During the present work we have taken profilograms of the obtained layers. They are shown in Fig. 6. It can be seen that the edge-growth effect is noticeable only in the case of GaAs deposition from gallium. The introduction of only 2.27 at % Bi to GaAs solution almost eliminates the edge-growth. We explain the phenomenon as follows.

The addition of bismuth to gallium causes a decrease of surface tension of the alloy $(Ga + Bi)^L$ with respect to pure gallium, because for bismuth $\sigma \simeq 390\,dyn\,cm^{-1}$ ($0.39\,N\,m^{-1}$) at 543 K [10] and for gallium $\sigma \simeq 640\,dyn\,cm^{-1}$ at 1073 K [11]. Therefore, the solution fills the column for alloys as shown in Fig. 5a and for Ga–As–Bi solution there are no conditions enabling the additional diffusion along the $Y$ direction. The studies carried out confirm the theory of two-dimensional diffusion of the layer edge-growth [12, 13].

Microscopic observations of the obtained layers

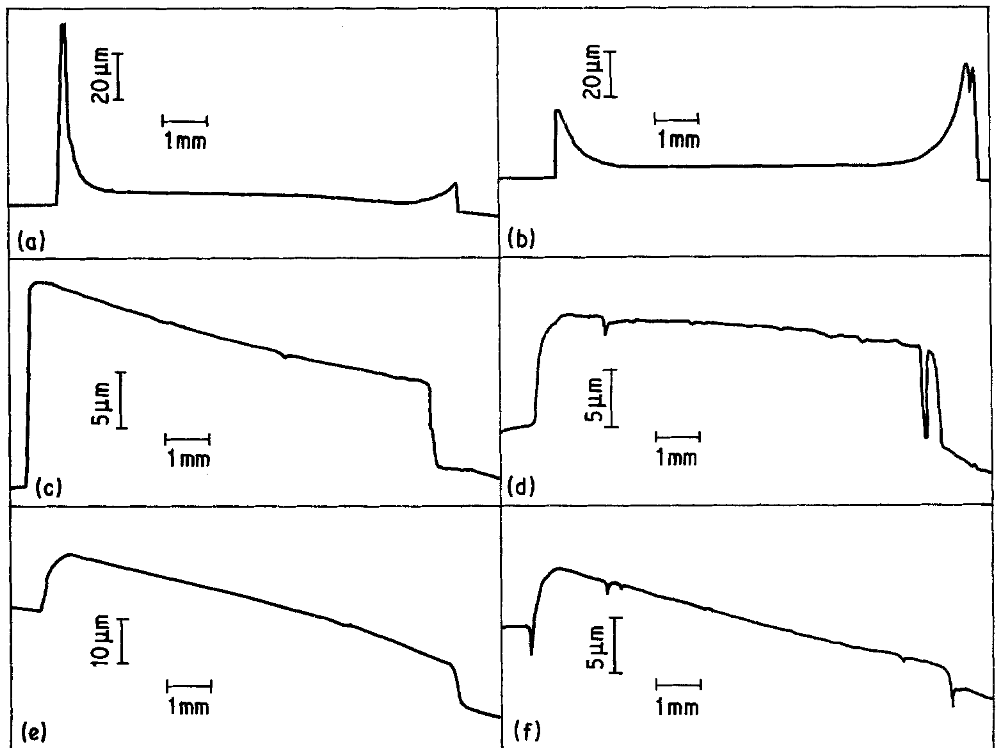


*Figure 6* Profilograms of GaAs epitaxial layers. (a) 97.9 wt % Ga, 2.1 at % As, $T_{p_1} = 1073\,K$, $t = 30\,min$; (b) 96.9 at % Ga, 3.1 at % As, $T_{p_2} = 1113\,K$, $t = 30\,min$; (c) 95.79 at % Ga, 1.94 at % As, 2.27 at % Bi, $T_{p_1} = 1073\,K$, $t = 30\,min$; (d) 2.01 at % Ga, 2.01 at % As, 95.98 at % Bi, $T_{p_1} = 1073\,K$, $t = 30\,min$; (e) 73.67 at % Ga, 2.53 at % As, 23.80 at % Bi, $T_{p_1} = 1113\,K$, $t = 30\,min$; (f) 2.01 at % Ga, 2.01 at % As, 95.98 at % Bi, $T_{p_1} = 1073\,K$, $t = 30\,min$.

have shown that in the case where Ga–As–Bi solutions are used during the deposition of GaAs, only single meniscus lines occur on the surface of the epitaxial layer. The surface has a bright polish and is free of defects.

## 4. Conclusions

The application of Ga–As–Bi solutions for the deposition of epitaxial layers

(i) eliminates edge-growth of the layers,

(ii) improves the morphology of the GaAs epitaxial layer surface, and

(iii) allows one to control the kinetics of layer growth by the composition of the liquid phase.

The conclusion is an additional confirmation of the two-dimensional diffusion theory of edge-growth.

It should be anticipated that the same effects can be achieved during the deposition of GaAlAs, for example, by using an addition of bismuth to the growth solution.

The existence of a maximum in the layer growth rate, within 2 to 10 at % Bi addition to the solution, requires additional studies for an explanation. In our opinion, the existence of a limited-solubility area in the liquid phase of the Bi–Ga system is responsible for this effect.

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