International Journal of Scientific Research and Management (IJSRM)
||Volume||10||Issue||08||Pages||MS-2022-69-74||2022||
Website: www.ijsrm.in ISSN (e): 2321-3418
DOI: 10.18535/ijsrm/v10i7.ms01

Perspectives of Double Feeding of the Melt Method on the Example of the Analysis of the InAs(1-x)–GaAs(x) Solid Solution Crystals Growth

Zaura Zakhrabekova, Vusala Kazimova, Elnara Islamzade, Akper Alekperov

Institute of Physics of Azerbaijan National Academy of Sciences
Baku, AZ-1143, H. Javid Ave., 131, Azerbaijan

Abstract
Using the example of InAs-GaAs system, the potential of double feeding of the melt method for growing single crystals of semiconductor solid solutions is shown. The concentration profiles of InAs-GaAs solid solutions crystals for certain modes of the considered method are calculated in Pfann approximation. In addition, under the same conditions, InAs-GaAs crystals were grown and their concentration profiles were determined. The results obtained give good agreement between the experimental and calculated data. It is shown that mathematical modeling of InAs-GaAs crystals growth by setting the crystallization and melt-feeding rates with constituent components makes it possible to obtain the required distribution of the main components in the direction of crystal growth, including uniform distribution, in the entire series of continuous InAs-GaAs solid solutions. The double feeding of the melt method is shown to be promising for obtaining single crystals of semiconductor solid solutions with a given concentration profile.

Keywords: InAs, GaAs, single crystal, solid solution, double feeding of the melt method.

Introduction

Among semiconductor materials, diamond-like semiconductor compounds of the AIII-BV type, as well as solid solutions based on them, are of particular scientific and practical interest in studying their properties. One of the solid solutions of this type that deserves special attention are InAs-GaAs crystals. InAs and GaAs completely dissolve in each other at any ratio, both in solid and liquid states [1]. This fact makes it possible to control the lattice parameters and the band gap by changing the composition of the matrix. The band gaps of the constituent components of this system differ by a factor of four (0.355 eV for InAs and 1.42 eV for GaAs). This makes it possible to create materials based on these solid solutions with desired properties in a wide range.

The main problem in the technology of growing semiconductor materials is the achievement of single-crystallinity of the obtained crystals. The most suitable method for achieving this result is the Czochralski method. However, the traditional method does not allow one to obtain single crystals of solid solutions of binary systems homogeneous in composition, due to the significant segregation of the main components in the process of melt crystallization [2]. There are various methods to eliminate the effect of component segregation on both the composition of the melt and the growing crystal [2–14]. The most effective among them is the modified Czochralski method - the double feeding of the melt method, which allows, by selecting the rates of feeding the melt with the main components and the rate of crystallization, to obtain homogeneous crystals of solid solutions of various compositions. In particular, this method has been successfully applied to grow homogeneous crystals of Ge-Si solid solutions [8].

Materials and Methods

On Figure 1 presents a conceptual scheme for growing single crystals of solid solutions by double feeding of the melt method [8]. From the moment of growth of a single crystal from an InAs-GaAs melt, rods of indium arsenide and gallium arsenide are introduced into it. During the entire cycle of growing a single crystal, the rates of crystallization and feeding of the melt with indium arsenide and gallium arsenide are maintained constant.

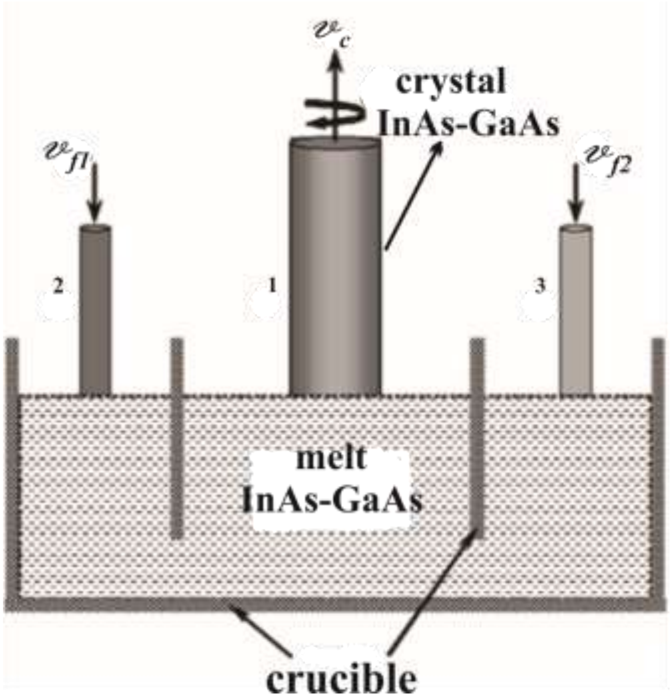

Figure 1: Conceptual diagram of growing crystals of solid solutions by double feeding of the melt method with constituent components. 1 – growing InAs-GaAs crystal, 2 and 3 – feeding rods of InAs and GaAs, respectively. V_{f1} and V_{f2} are the rod insertion rates, V_c is the pulling rate of the InAs-GaAs crystal.

Results and Discussion

Mathematical modeling of the concentration profile

In this work, a mathematical calculation of the necessary technological parameters for the growth of single crystals of solid solutions of a given composition by double feeding of the melt method as applied to the InAs-GaAs system is carried out. The goal is to establish optimal conditions for growing single crystals of InAs-GaAs solid solutions with a given concentration profile.

The problem of distributing the concentration of the second component along the crystal axis was solved in the Pfann approximation: there is no evaporation of components in the melt; the crystallization front is flat; the diffusion of In and Ga atoms in the growing crystal is negligibly small; the diffusion rates of atoms of the constituent components in the melt are quite high and ensure the uniformity of its composition throughout volume; at the crystallization front there is an equilibrium between the solid and liquid phases, determined by the phase diagram [2-4]. Taking GaAs as the second component, we introduce the following designations: V_m^0 and V_m are the volumes of the melt in the crucible at the initial and current moments, V_c is the volume of the crystallizing melt per unit time, V_1 and V_2 are the volumes of feeding InAs and GaAs ingots introduced into melt per unit time, C_{2m} and C_{2c} are the concentrations of atoms of the second component in the melt and crystal, respectively, C is the total amount of the second component in the melt, $K=C_{2c}/C_{2m}$ is the equilibrium segregation coefficient of the second component. Using the above notation, we can write the following:

$$C_{2m} = \frac{C}{V_m} \qquad \text{and} \qquad \frac{dC_{2m}}{dt} = \frac{\dot{C}\,V_m - \dot{V}_m C}{V_m^2} = \frac{\dot{C} - \dot{V}_m C_{2m}}{V_m} \qquad (1)$$

By the condition of the problem, V_c, V_1 and V_2 do not depend on time and in this case have place the following equations:

$$V_m = V_m^0 - (V_c - V_1 - V_2)t \qquad \dot{V}_m = V_1 + V_2 - V_c \tag{2}$$

Substituting (2) in (1) and solving the latter, we have:

$$\gamma = \frac{1}{1-\alpha-\beta}\left\{1 - \exp\left[-\int_{C_{2m}^0}^{C_{2m}} \frac{(1-\alpha-\beta)dC_{2m}}{\alpha - C_{2m}(K-1+\alpha+\beta)}\right]\right\} \tag{3}$$

Here $\alpha = V_2/V_c$, $\beta = V_1/V_c$, $\gamma = V_c t/V_m^0$.

The growth of homogeneous single crystals of solid solutions will take place at a constant melt composition with time, i.e. at $dC_{2m}/dt=0$. Then from (1) and (2) we obtain the required values of the initial compositions of the melt for the corresponding values of α and β and vice versa, at which completely homogeneous crystals grow.

$$C_{2m}^* = \frac{\alpha}{K-1+\alpha+\beta} \tag{4}$$

In this case, for the concentration of the second component in a growing crystal, we have:

$$C_{2c}^* = \frac{K\alpha}{K-1+\alpha+\beta} \tag{5}$$

An analysis of this equation shows that the growth of homogeneous crystals can be ensured both at K>1 and at K<1. According to (5), the calculation of C_{2m}^* and C_{2c}^* dependences on α and β requires knowledge of K in the entire range of component concentrations, which can be determined from the phase diagram of the system. Having set a specific value of α + β, for the required composition of the crystal we determine the corresponding value of K from the phase diagram of the InAs-GaAs system. Then, using equation (5), we find α and β. The values of α and β calculated in this way for various given values of C_{2m}^* in the range 0<x<1 determine the dependence of the equilibrium concentration of the crystal on α and β. On the Figure 2 shows these graphs, using the example of three different values of α + β.

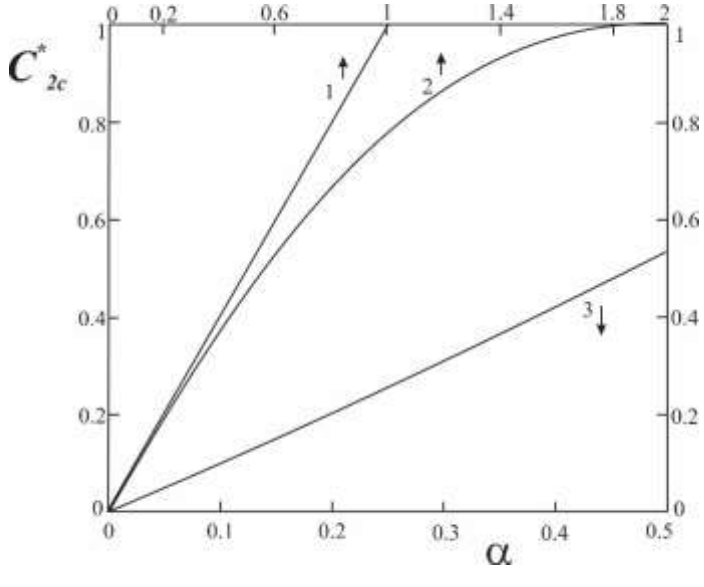

Figure 2: Dependence of the composition (C^*_{2c}) of a homogeneous InAs-GaAs crystal on α (GaAs is the second component with K>1) grown by the double feeding of the melt method. 1) $\alpha+\beta=1$; 2) $\alpha+\beta=2$; 3) $\alpha+\beta=0.5$

Here, in the calculations, GaAs with K>1 is taken as the second component. Obviously, similar graphs can be constructed for the case when the second component is InAs with K<1. Graphs on Figure 2 determine the starting composition of melt and the ratio of the rates of feeding and crystallization of the melt to grow homogeneous InAs-GaAs crystals with a given composition. As can be seen, by changing α , β and α + β, it is possible to obtain homogeneous crystals of solid solutions in various modes in the entire range of InAs and GaAs concentrations.

On Figure 3 shows the dependences of C^*_{2c} on α obtained from formula (5) at various values of β

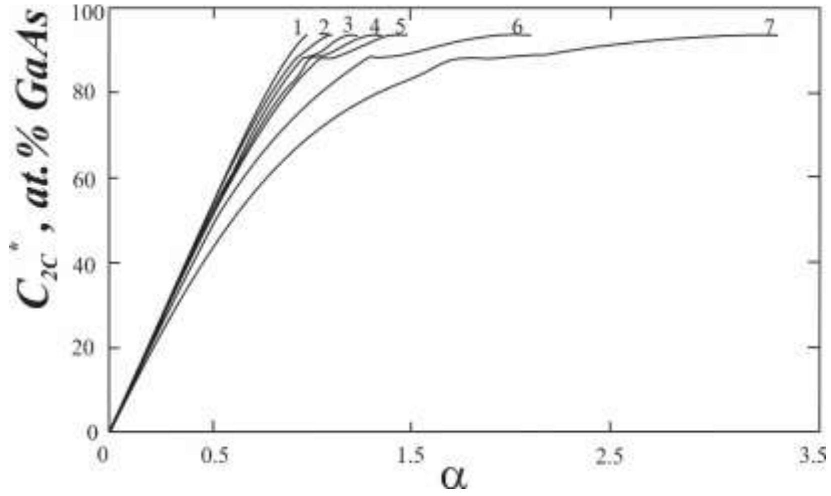

Figure 3: Dependence of C^*_{2c} on α for InAs-GaAs crystals grown by double feeding of the melt method. 1- β=0.1, 2- β=0.2, 3- β=0.3, 4 - β=0.4, 5- β=0.5, 6- β=1, 7- β=2.

On Figure 4 shows the calculated dependences of the second component concentration in atomic percent, on γ in InAs-GaAs crystals grown by double feeding of the melt method in three different modes. The initial

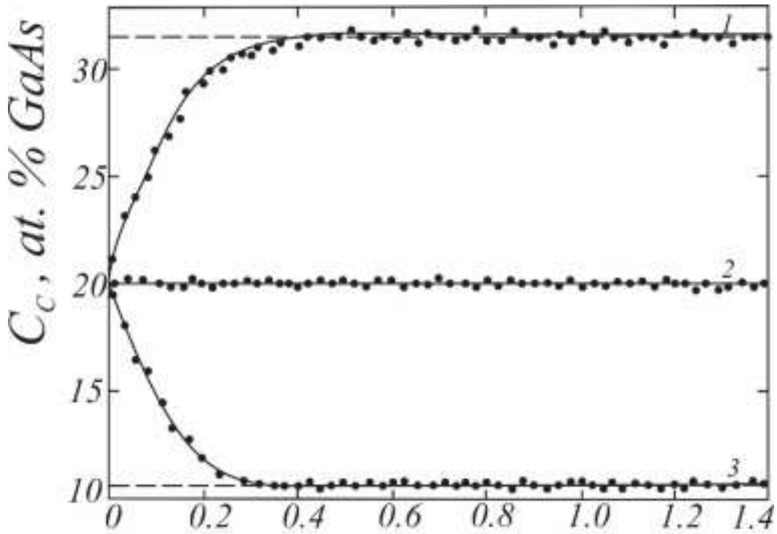

Figure 4: Graphs of the concentration of the second component in atomic percent, from γ in InAs-GaAs crystals grown by double feeding of the melt method under three different modes. The initial composition of the melt in all cases is $InAs_{0.8}$-$GaAs_{0.2}$. Lines - calculated data: 1 and 3 correspond to the modes at α = 0.3,

β = 0.1and α = 0.1, β = 0.3; 2 corresponds to the uniform growth of $InAs_{0.8}$-$GaAs_{0.2}$ crystals. Circles are experimental data.

composition of the melt is the same in all cases and corresponds to $InAs_{0.8}$-$GaAs_{0.2}$. Lines 1 and 3 are calculated by formula (3) and correspond to the modes at α= 0.3, β= 0.1 and α= 0.1, β= 0.3, respectively. In the first mode, there is an increase, and in the third, a decrease in concentrations to values that satisfy equation (5) with the corresponding α and β. In the future, a completely homogeneous crystal grows. Line 2 corresponds to the uniform growth of $InAs_{0.8}$ -$GaAs_{0.2}$ crystals at values of α and β satisfying expression (5) for the growth of InAs-GaAs solid solution crystals with 20% gallium arsenide content.

In the modes used by us in mathematical calculations (Fig. 4(1,3)), InAs-GaAs crystals were grown by double feeding of the melt method. A homogeneous $InAs_{0.8}$-$GaAs_{0.2}$ crystal (Fig. 4(2)) was grown at α=0.2 and β=0.8. The obtained ingots were cut in the axial direction into pieces 1 mm wide, the specific gravity of which was used to determine the concentration profiles of the grown crystals. In Figure 4, these data are shown in circles. As we can see, the experimental results show good agreement with the theoretical calculations.

Conclusions

Our studies show that the mathematical modeling of the concentration profiles of the main components in crystals of solid solutions grown by double feeding of the melt method works well not only for Ge-Si crystals, but also for the InAs-GaAs system. This allows us to assume that these calculations can also be successfully applied to all crystals of solid solutions based on AIII-BV diamond-like compounds.

A significant disadvantage of the method of double feeding of the melt with constituent components is the need for prefabrication of macrohomogeneous InAs and GaAs polycrystalline rods often InAs-GaAs polycrystalline rods of different composition, which, as noted in the literature [8], is a rather complex technological problem. In addition, during the manufacturing process of feed rods, uncontrolled impurities are inevitably introduced into them, polluting the material.

In the case of double feeding of the melt with the rods of the constituent components, the homogeneity of the composition of the material introduced into the melt is fully guaranteed. The composition of the growing homogeneous single crystal is then controlled by a simple change in the rate of pulling the crystal out of the melt and the rates of introduction of the feed rods into the melt.

Based on the foregoing, the following conclusion can be drawn. The method of continuous double feeding of the melt with rods of constituent components, at appropriate values of the rate of crystallization and the rates of feeding of the melt with constituent components, provides the growth of single crystals of solid solutions uniform over the entire length in the entire continuous series of compositions, which indicates the prospects for using this method to grow single crystals of solid solutions.

Ethics approval and consent to participate

Not applicable

Conflicts of Interest

The authors declares that there is no conflict of interest regarding the publication of this paper.

Funding Statement

The research was carried out based on the Institute of Physics of ANAS.

Authors' contributions

ZZ and VK carried out mathematical modelling of the concentration profiles of InAs-GaAs crystals grown by double feeding of the melt method.

AA obtained InAs-GaAs crystals by double feeding of the melt method. EI experimentally determined the axial distribution of the main components in the grown crystals.

References

1. R. A. Smith, “Semiconductors”, *Cambridge University Press*; First. edition (January 2, 1959)
2. QingLi Zhang, ShaoTang Yin, DunLu Sun, SongMing Wan, “Segregation during crystal growth from melt and absorption cross section determination by optical absorption method”, Science in China Series G: Physics, Mechanics and Astronomy, vol. 51, pp. 481–491, 2008. https://link.springer.com/article/10.1007/s11433-008-0064-z
3. G. Kh. Azhdarov, T. Kucukomeroglu, A. Varilci et al., “Distribution of components in Ge–Si bulk single crystals grown under the continuous feeding of the melt with the second component (Si)”, *Journal of Crystal Growth*, vol. 226, no. 4, pp**.** 437-442, 2001. https://www.sciencedirect.com/science/article/pii/S0022024801012702
4. T.A. Campbell, M. Schweizer, P. Dold et al., “Float zone growth and characterization of $Ge_{1-x}Si_x$ ($x \leqslant 10$ at%) single crystals”, *Journal of Crystal Growth*, vol. 226**,** no. 2-3, pp. 231-239, 2001. https://www.sciencedirect.com/science/article/pii/S002202480101394X
5. K. Nakajima, T. Kusunoki, Y. Azuma et al., “Compositional variation in Si-rich SiGe single crystals grown by multi-component zone melting method using Si seed and source crystals”, *Journal of Crystal Growth*, vol. 240**,** no. 3-4, pp. 373-381, 2002. https://www.sciencedirect.com/science/article/pii/S0022024802009405
6. A. Dahlen, Fattah, G. Hanke, Karthaus, “Bridgman and Czochralski growth of Ge-Si alloy crystals” *Cryst. Res. Technol.* vol. 29, no. 2, pp. 187-198, 1994. https://onlinelibrary.wiley.com/doi/abs/10.1002/crat.2170290206
7. N.V. Abrosimov, S.N. Rossolenko, W. Thieme et al., “Czochralski growth of Si- and Ge-rich SiGe single crystals”, *Journal of Crystal Growth*, vol.174**,** no. 1-4, pp. 182-186, 1997. https://www.sciencedirect.com/science/article/pii/S0022024896011025
8. G. Kh. Azhdarov, Z. M. Zeynalov, Z. A. Agamaliyev, A. I. Kyazimova, “Growth of Single Crystals of Semiconductor Solid Solutions by Double Feeding of the Melt Method”, *Crystallography Reports*, vol. 55, no. 4, pp. 716-719, 2010. https://link.springer.com/article/10.1134/S1063774510040309
9. Z. A. Agamaliyev, M. A. Ramazanov, G. Kh. Azhdarov, “A Model for Crystal Growth of Solid Solutions in the InAs–GaAs System by a Modified Floating-Zone Technique”, *Inorganic materials*, vol. 55, no. 3, pp. 205-209, 2019. https://link.springer.com/article/10.1134/S0020168519030014
10. З.М. Захрабекова. *Кристаллы твердых растворов Ge-Si: Получение и электрические свойства твердых растворов сложнолегированных кристаллов Ge-Si с примесями меди, алюминия и сурьмы*, (Германия: Lambert Akademic *Publishing, 2013).*
11. Z.A. Agamaliyev, E.M. Islamzade, G.Kh. Azhdarov, “Modeling the distribution of Ga and Sb impurities in Ge–Si single crystals grown by double feeding of the melt: Growth conditions for homogeneous single crystals”, *Crystallography Reports*, vol. 61, no. 2, pp. 327- 330, 2016. https://link.springer.com/article/10.1134/S1063774516020024
12. G. Azhdarov, R. Kyazimzade, “Growth of homogeneous single crystals of GeSi solid solutions using a Ge seed by the modified Bridgman method”, *Crystallography Reports*. vol. 50, no. 1, pp. S149-S151, 2005. https://link.springer.com/article/10.1134/1.2133992
13. G.Kh. Azhdarov, Z.A. Agamaliev, E.M. Islamzade, “Hybrid technique for growing homogeneous single crystals of semiconductor solid solutions from melt”, *Crystallography Reports*, vol. 59, no. 3, pp. 442-445, 2014. https://link.springer.com/article/10.1134/S1063774514020059
14. Hiroki, Miyata, “Crystallographic investigation of homogeneous SiGe single crystals grown by the traveling liquidus-zone method”, *Journal of Crystal Growth*, vol. 303, no. 2, pp. 607-611, 2007. https://www.sciencedirect.com/science/article/pii/S0022024807000516