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PECULIARITIES OF LOW-TEMPERATURE GALLIUM ARSENIDE CRYSTALLIZATION UNDER VARYING COOLING RATES

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Abstract The parameters of GaAs epitaxial layers grown by the low-temperature LPE method in the temperature range of 600–500 °C under varying cooling rates and different degrees of supercooling (5 °C, 10 °C, and 15 °C) of the gallium solution-melt were calculated. To achieve maximum cooling rates, a method involving the introduction of a cold body above the graphite cassette was used to cool the substrate–melt interface, enabling a change in the cooling rate from 5 °C/min to 14 °C/min within 230 seconds. It was found that under these conditions, it is possible to crystallize layers with maximum thicknesses of 7.5 µm, 10 µm, and 12 µm, respectively. The obtained theoretical results show good agreement with experimental data. The crystallized GaAs epitaxial layers can be used in the fabrication of various terahertz-range devices.

Keywords: gallium arsenide, epitaxial layer, variable cooling rate, terahertz range.

1. Introduction

Low-temperature gallium arsenide (LT-GaAs) is a special type of gallium arsenide grown using molecular beam epitaxy (MBE) or other methods at low temperatures (approximately 200–300 °C) [1–2]. The growth conditions associated with these methods result in the generation of a high concentration of vacancies and interstitial atoms, which in turn determine its unique galvanomagnetic properties, such as ultrashort time of carrier relaxation (for both electrons and holes) and high specific resistivity [3]. These characteristics make LT-GaAs a promising material for the fabrication of various terahertz-range devices [4].

An alternative approach to producing LT-GaAs is low-temperature liquid-phase epitaxy (LT–LPE). Since this method ensures near-equilibrium crystallization conditions [5], achieving high-resistivity layers requires a different approach – one that accounts for the formation of specific electrophysical and structural properties at low temperatures and under minimal supersaturation of the group V element in the growth environment. The focus should be placed on forming layers with a high concentration of point and complex defects, as well as various types of structural imperfections, including microinclusions of dopant elements. Collectively, this defect ensemble should ensure both high specific resistivity and minimal charge carrier lifetime in the resulting material.

To achieve the desired properties of LT-GaAs, low-temperature liquid-phase epitaxy (LT-LPE) can be employed. Unlike traditional methods, this approach involves crystallization of the layers under variable cooling rates. This leads to the creation of more non-equilibrium growth conditions and a significant increase in the segregation coefficients of background and intentional dopants, which, in combination, should help address the challenge of forming LT-GaAs layers with high specific resistivity and short charge carrier lifetimes.

In conventional LPE, various crystallization modes exist, including gradual cooling from a saturated melt, growth from a supersaturated melt, and rapid cooling from a supersaturated melt [6]. These modes typically use a constant cooling rate. The crystallization mode proposed here for LT-GaAs is based on a variable cooling rate, which sharply increases from approximately 1 °C/min to 10–15 °C/min to establish more non-equilibrium growth conditions. To determine the optimal technological parameters for such a process, it is necessary to perform model calculations of arsenic diffusion and distribution across the thickness of the growth gap in order to evaluate the crystallization rates of the layers under these conditions.

2. Experimental procedure

The temperature-time profile of GaAs epitaxial layer growth under variable crystallization rate is shown in Fig. 1.

During the time interval $t_0 - t_1$, the reactor with the graphite cassette is heated from room temperature to 630 °C. At this temperature, homogenization of the gallium solution-melt is carried out for no less than one hour. At time t_2, a rapid temperature drop is initiated at a rate of 5 °C/min, which is the maximum controllable cooling rate achievable with our equipment. At this rate, the temperature profile in the working zone of the thermal block remains uniform with an accuracy of ±0.5 °C.

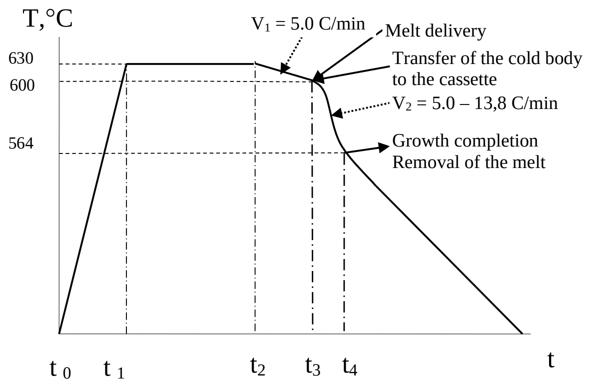
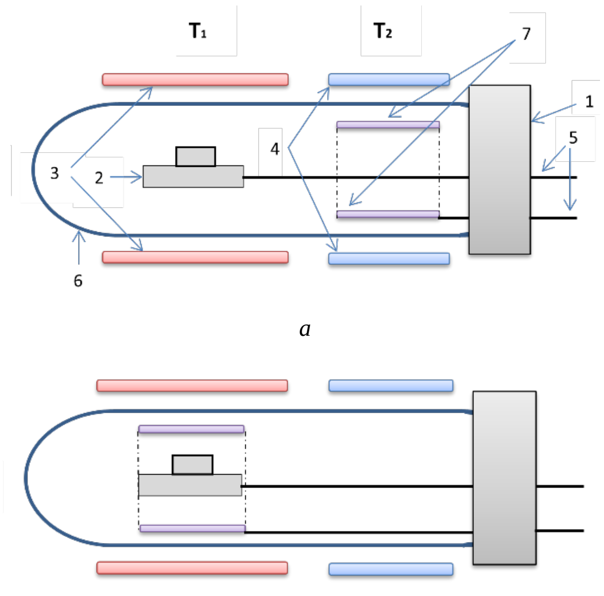


Fig. 1. Temperature-time profile of GaAs epitaxial layer growth under variable crystallization rate



a

b

Fig. 2. Hardware setup of the cooling method for a saturated solution-melt used in the crystallization of GaAs layers by introducing a cold body into the reactor's working zone: 1 – shutter for sealing the quartz reactor; 2 – graphite cassette; 3 – working temperature zone (T_1); 4 – auxiliary temperature zone ($T_2 < T_1$); 5 – molybdenum rod; 6 – quartz reactor; 7 – graphite cylinder (cold body).

At time t_3, the cooling rate reaches 5 °C/min. At this point, the gallium solution-melt, which may be supersaturated by 5 °C, 10 °C, or 15 °C, is applied to the gallium arsenide substrate. Crystallization of the epitaxial layer begins. Simultaneously, to ensure a sharp increase in the crystallization rate, a cold body – a graphite cylinder with a mass of approximately 2.5 kg and a temperature of about 100 °C (taken from the reactor's cold zone) – is moved into the working zone of the quartz reactor, fully covering the graphite cassette. This causes a rapid cooling of the cassette. The hardware setup of this cooling method for the saturated gallium solution-melt is shown in Fig. 2.

The temperature change inside the graphite cassette follows the temperature profile shown in Fig. 3. From the figure, it is clear that within 250 seconds, there is a sharp increase in the cooling rate from 5 °C/min to 13.8 °C/min. After that, the cooling rate of the cassette gradually decreases to the controlled cooling rate of the reactor of 5 °C/min.

During the time period from t_3 to t_4, the epitaxial layer crystallizes as the cooling rate sharply changes from 5 °C/min to 13.8 °C/min. At the moment t_4, at a temperature of 564 °C, the solution-melt is removed from the surface of the substrate. The crystallization of the layer stops. The reactor with the graphite cassette is then cooled to room temperature.

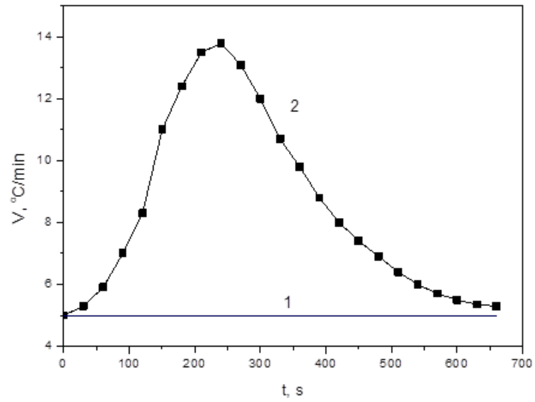


Fig. 3. Temperature change inside the graphite cassette after placing the cold object on the cassette.

A key aspect in forming GaAs layers suitable for use in terahertz devices is the significant concentration of defects of various natures, which can substantially reduce the lifetime of the main carriers and increase the specific resistance. In low-temperature rare-phase epitaxy, this can be achieved if during the growth process the segregation coefficients of both background and specially introduced dopants can be influenced. The main technological parameter that can provide this influence is the crystallization rate of the layers which is proportional to the cooling rate of the substrate-saturated solution-melt system. The results obtained by the authors in forming sharp concentration profiles at the substrate-epitaxial layer interface in the epitaxial structure of GaAs substrate – GaAs epitaxial layer have confirmed this [7]. The effective segregation coefficient of the dopant depends only on the crystallization rate (within the selected temperature range), which is an argument in the exponential dependence. Therefore, a change in the crystallization rate significantly affects the value of the effective dopant segregation coefficient [8]. This effect is the basis of the proposed approach for controlling the ensemble of point defects, which determine the electrophysical and structural properties of epitaxial layers. According to this approach, the epitaxial layer should crystallize within a certain temperature range with a variable crystallization rate. If the crystallization interval spans several tens of degrees, then the change in crystallization rate should be as large as possible to significantly affect the properties of the crystallized layers. This requirement is especially important when forming layers at low crystallization temperatures.

To select the optimal technological conditions for the crystallization of epitaxial layers with a varying crystallization rate, it is necessary to calculate the dependencies of the layer thicknesses on the time of crystallization from the supersaturated solution-melt according to the sharp cooling mode [6] which ensures the maximum crystallization rate. The input data for the calculation include the temperature range for epitaxial layer growth (600–500 °C), the degree of supercooling of the solution-melt (5–15 °C) before contact with the substrate, the thickness of the growth gap (1 mm), and the solubility of arsenic in gallium within the selected temperature range for calculations [6]. The expression used for calculating the thickness is [6]:

$$d = \left(\frac{1}{C_{As}^{S} m}\right) \cdot \left(\frac{\mathrm{D}}{\pi}\right)^{\frac{1}{2}} \cdot [2\Delta T t^{\frac{1}{2}} + \left(\frac{4}{3}\right) R t^{3/2}, (1)$$

where d is a thickness of the epitaxial layer, µm; C_{As}^{S} is the concentration of As atoms in the solid phase, at/sm^3; m is a slope of the liquidity curve at the point T_2; D is a diffusion coefficient, m^2/s; ΔT is a temperature difference, K; t is growth time, s; R is a cooling rate, °C/min;

The concentration of arsenic in the solid phase was calculated according to the expression:

$$C_{As}^{S} = \frac{4}{a_0^3}, \tag{2}$$

and the slope of the liquidity curve is:

$$m = \frac{T_2 - T_1}{C_{As}^{l}(T_2) - C_{As}^{l}\,(T_1)}, \tag{3}$$

where m is the slope of the liquidity curve at temperature T_2; $C_{As}^{l}(T_2)$ is the concentration of As in the liquid phase at temperature T_2; $C_{As}^{l}\,(T_1)$ is the concentration of As in the liquid phase at temperature T_1.

The concentration of arsenic in the liquid phase at temperatures T_1 and T_2 was determined by the following formulas

$$C_{As}^{l}(T_2) = \frac{M \cdot X_{As}(T_2) \cdot N_A}{M_{As}} \tag{4}$$

$$C_{As}^{l}(T_1) = \frac{M \cdot X_{As}(T_1) \cdot N_A}{M_{As}}$$

where M is the molar mass of the solution; M_{As} is the molar mass of As; N_A is Avogadro's number; X_{As} (T_2) is the atomic fraction of As at temperature T_2 (obtained from the system state diagram Ga-As [6]); X_{As} (T_1) is the atomic fraction of As at temperature T_1 (obtained from the system state diagram Ga-As [6]).

The MathCad software package (MathCad, version 15.0, PTC Inc., USA) was used to process data and perform calculations, which allowed for implementing all the necessary mathematical models and checking the correctness of calculations. The OriginPRO software package (OriginLab Corporation, version 2024, USA) was used to visualise the results in the form of curve graphs.

3. Experimental results and discussion

Figs. 4–6 present the calculations of the dependency of the thickness of gallium arsenide epitaxial layers on the crystallization time within the temperature range of 600–550 °C, for various degrees of supercooling (5–15 °C) of the gallium solution-melt. The data shown in the figures testify that for short growth times (50–100 seconds) the layer thickness is not significantly dependent on the crystallization rate, changing little even when the degree of supercooling is varied from 5 °C to 15 °C. Increasing the crystallization time leads to a significant increase in layer thickness, especially when the cooling rate is increased to (10–15) °C/min.

For example, at a degree of supercooling of the gallium solution-melt ΔT = 5 °C and a cooling rate of 15 °C/min (Fig. 4), increasing the growth time from 50 to 400 seconds allows for the growth of layers with a thickness of approximately 12 µm. Therefore, the obtained calculations of the layer thickness dependence on the crystallization rate show that at higher rates thicker layers can be achieved at lower crystallization temperatures. The degree of supercooling of the melt is also an important factor influencing the layer thickness under otherwise identical conditions. If the supercooling of the melt ΔT increases from 5 °C to 15 °C, the thickness of the layers crystallized over 400 seconds increases from 12 µm to 20 µm (Figs. 4 and 6).

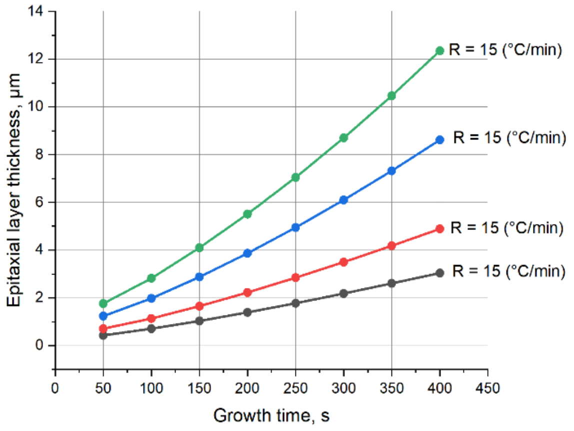


Fig. 4. Dependence of the thickness of epitaxial GaAs layers on the crystallization time at different fixed cooling rates and the supercooling of the gallium melt solution ΔT = 5 °C.

Considering the obtained data, it is necessary to estimate the maximum possible thickness of layers that can be achieved under the conditions of rapid cooling from a supersaturated solution-melt with a variable crystallization rate. Fig. 7 shows the dependence of the thickness of epitaxial GaAs layers on crystallization time, with cooling rates varying from 5 °C/min to 14 °C/min for different degrees of supercooling of the solution-melt. The calculations were carried out for crystallization times up to 250 seconds. This time was determined from the experimental graph (Fig. 3) showing the change in the cooling rate of the graphite cassette after the cold body being moved onto the cassette. During this period, the cooling rate increases from the equilibrium value of 5 °C/min to a maximum of 14 °C/min. Precisely under the condition of rapid increase in the cooling rate the most non-equilibrium growth conditions are created, allowing for the formation of a significant number of defects in the layers. If the crystallization time exceeds 250 seconds, the cooling rate gradually decreases to the equilibrium rate being maintained by the equipment.

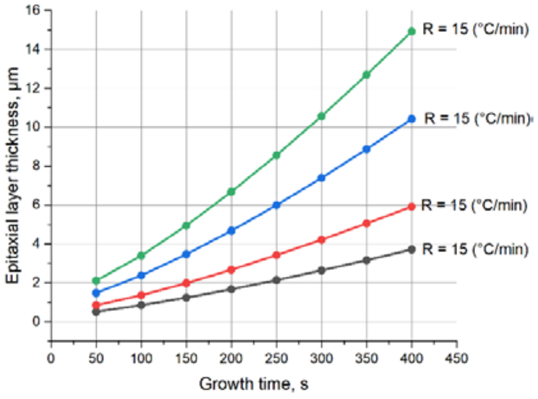


Fig. 5. Dependence of the thickness of epitaxial GaAs layers on the crystallization time at different fixed cooling rates and the supercooling of the gallium melt solution ΔT = 10 °C.

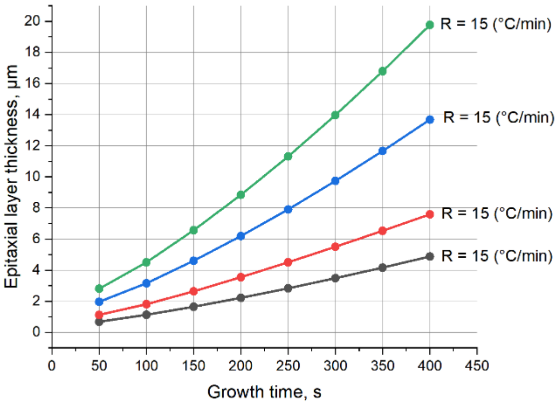


Fig. 6. Dependence of the thickness of epitaxial GaAs layers on the crystallization time at different fixed cooling rates and the supercooling of the gallium melt solution ΔT = 15 °C.

As shown in Fig. 7, all the curves have a concave and a convex section, with an inflection point around 150 seconds. After the supersaturated melt coming into contact with the substrate, the growth rate during the first several tens of seconds is determined by the arsenic gradient formed as a result of the initial supercooling of the melt. In curves 1–3 (Fig. 7), the dependence of layer thickness on growth time is nearly linear during the first 100 seconds of crystallization. During this time, the cold impulse reaches the melt, causing a sharp increase in the cooling rate. This leads to an increase in the arsenic gradient in the growth gap and, consequently, to an increase in the flux of arsenic atoms toward the growth interface.

The crystallization rate increases sharply, which is observed as a rapid increase in layer thickness for crystallization times exceeding 100 seconds. After reaching the maximum cooling rate at approximately 230 seconds and its subsequent decrease, the crystallization rate quickly declines. The dependence of layer thickness on growth time approaches saturation.

The increase in cooling rate is accompanied by an increase in layer thickness. The maximum thickness of 2 μm can be achieved at a melt supercooling of 15 °C. The calculated results (solid curves) show good agreement with the experimental data (dotted curve).

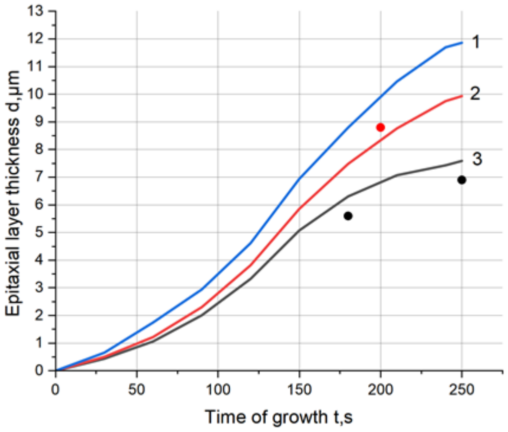


Fig. 7. Dependence of the thickness of epitaxial GaAs layers on the crystallisation time when the cooling rate is changed from 5 °C/min to 14 °C/min for different values of the supercooling of the melt solutions: 1 – 15 °C; 2 – 10 °C; 3 – 5 °C. Solid curves – calculation, dotted curve – experiment.

4. Conclusions

The formation of the properties of GaAs layer suitable for use in the terahertz range by the LPE (Liquid Phase Epitaxy) method requires the application of non-standard crystallization modes that ensure highly non-equilibrium growth conditions. Technological parameters that can enable this include low temperatures, maximum supercooling of the melt, and high crystallization rates. To select the optimal technological conditions for the growth of the epitaxial layer under variable crystallization rates, calculations were performed for determining the dependence of layer thickness on crystallization time under the rapid cooling condition from a supersaturated solution-melt.

The main parameter that most significantly affects the electrophysical and structural properties of the layers is the cooling rate of the melt-substrate system. To achieve maximum cooling rates, the method involving the use of a cold body for rapid cooling of the melt-substrate system was selected, which allows the increase in the cooling rate from 5 °C/min to 14 °C/min within 230 seconds.

The calculated dependencies of the thickness of the GaAs epitaxial layer on crystallization time for various supercooling levels of the melt (5 °C, 10 °C, 15 °C) show that under these conditions, it is possible to crystallize layers with maximum thicknesses of 7.5 µm, 10 µm, and 12 µm, respectively. The calculated results are in good agreement with experimental data.

Thus, it is demonstrated that at low epitaxy temperatures (600–500 °C), it is possible to crystallize GaAs epitaxial layers while maintaining highly non-equilibrium crystallization conditions for at least 230 seconds of growth. This growth mode promotes the generation of a significant number of defects, thereby enabling the crystallization of layers with high specific resistivity and short charge carrier lifetimes. The resulting GaAs layers can be used in the production of various terahertz-range devices.

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ОСОБЛИВОСТІ КРИСТАЛІЗАЦІЇ НИЗЬКОТЕМПЕРАТУРНОГО АРСЕНІДУ ГАЛІЮ ЗА ЗМІННИХ ШВИДКОСТЕЙ ОХОЛОДЖЕННЯ

Семен Круковський, Владислав Аріков

Виконано розрахунок параметрів епітаксійних шарів GaAs, отриманих методом низькотемпературної РФЕ у температурному діапазоні 600–500 °C за змінних швидкостей охолодження і різних значень переохолодження (5 °C, 10 °C і 15 °C) розчину-розплаву галію. Для забезпечення максимальних швидкостей охолодження використано методику введення холодного тіла над графітовою касетою для охолодження границі розділу підкладка – розплав, яка забезпечила зміну швидкості охолодження від 5 °C/хв до 14 °C/хв за 230 с. Встановлено, що за таких умов можуть кристалізуватись шари з максимальними товщинами 7,5 мкм, 10 мкм і 12 мкм відповідно. Розрахункові результати добре узгоджуються з експериментальними даними. Отримані шари GaAs можна використовувати для виготовлення різноманітних приладів терагерцового діапазону.

Semen Krukovskyi – D. Sc., Professor, Head of the Department of Semiconductor Materials and Devices, Research and Production Enterprise “Electron-Carat”. The main areas of scientific activity of prof. S. Krukovsky include the technology of obtaining device epitaxial structures A_3B_5 by liquid-phase and gas-phase epitaxy methods and devices based on them. Professor Krukovsky is the author of more than 110 scientific publications indexed in the scientometric databases Scopus and Web of Science and more than 20 certificates for inventions and patents. More than 20 scientific research works have been carried out under his leadership.

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