Features of Low-Temperature GaAs Formation for Epitaxy Device Structures

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This article presents the results on the peculiarities of the formation of low-temperature gallium arsenide under the influence of complex earth elements ytterbium and aluminum. The physical properties of the epitaxial layers were investigated by ECV profiling, and the structural characteristics using XRD. It is shown that at certain optimal concentrations of ytterbium (3.0-3.2)·10−3 at.% and aluminum (1·10−4 at.%) it is possible to obtain structurally perfect GaAs epitaxial layers with a low concentration of carriers, and modulation of the rate of temperature decrease allows to obtain a sharper interface between layers with different doping levels. Such layers can be used in photodiode or microwave structures. It is established that an increase in the concentration of ytterbium in the melt causes deterioration of the structural properties of the layers due to the generation of additional defects, which can be used to create optoelectronic devices in the terahertz range.

Keywords: Gallium arsenide, Rare-earth element, Profile of charge carrier distribution, Interface, Terahertz range devices.

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1. INTRODUCTION

Low temperature gallium arsenide (low-temperature grown GaAs, LT-GaAs) may have several applications in epitaxial device structures: as an active layer in Gunn diodes, or terahertz devices, or thin-film solar cells. For each of these types of devices, its characteristics may differ significantly or even be incompatible.

For example, photocathode antennas based on semiconductor materials with a short lifetime of nonequilibrium charge carriers (picoseconds or less) are used to generate and detect terahertz radiation [1]. This can be achieved if LT-GaAs has a significant number of structural point defects or imperfections in the form of deep centers [2]. In LT-GaAs, the concentration of these defects may be about 10^{20} cm^{−3} [3]. If their concentration is increased, the characteristics of optoelectronic devices in the terahertz range can be improved. On the other hand, in Gunn diodes or p-i-n photodiode structures [4], the active layer should be characterized by a low concentration of carriers, and most importantly their high mobility, which can be achieved only in structurally perfect layers with a low concentration of defects of various origins. From this point of view, the search for a universal technical approach to solving such diverse problems is interesting.

One of such solutions is the use of complex (contemporary) doping with rare earth elements (REE) and isovalent impurity (IVI) in the process of growth by low-temperature liquid-phase epitaxy (LTLPE). Objective prerequisites for this are: 1) Low crystallization rates, which are comparable to those achieved by the methods of MBE (molecular-beam epitaxy) and MOSVD (metal-organic vapor-phase epitaxy) at reduced pressures. 2) Only the method of liquid-phase epitaxy of A3B5 materials can most fully ensure the achievement of all the advantages of doping with REE, the main of which is the reproducible and predictable control of defective-impurity structure of semiconductors [5, 6]. Unlike other technological methods, where the role of REE is reduced to the generation of uncontrollable impurities in the semiconductor matrix, in RFE, most uncontrolled impurities remain outside the semiconductor in the melt solution as REE compounds, and only a small number of REE atoms can enter the REE crystal lattice, where it acts as a heteropitaxy center.

The aim of this work is to investigate the influence of complex doping of REE and IVI on the electrophysical parameters and structural perfection of epitaxial layers LT-GaAs obtained by LTLPE from the point of view of their application in various device structures of microelectronics.

2. EXPERIMENTAL

Samples used in this study were grown by LTLPE. GaAs epitaxial layers were formed in a graphite cassette from molten Ga (99.9999 %, CMK Ltd) and polycrystalline GaAs (99.9999 %, CMK Ltd, free electron concentration (5-7)·10^{15} cm^{−3}) They contained 1-4 µm thick n-GaAs or p-GaAs epilayers on (100)-oriented n-GaAs:Sn (9·10^{17} cm^{−3}, 2.0·10^{18} cm^{−3}) substrates grown from Ga solution-melts doped with Yb (3.0-4.5)·10^{−3} at. % and Al (1·10^{−3} at. %). Both Al and Yb were added to the batch just before the cassette was loaded.

The temperature range of epitaxial growth was 610-600 °C, the cooling rate was 1.5 °C/min. The growth gap in all experiments was 1 mm.

Working out of technological modes for the formation of a sharp profile of the electron concentration distribution at the interface of n-GaAs/n+ -GaAs layers was carried out in the same temperature range at rates

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of temperature decrease of 0.3 °C/min and 1.5 °C/min. Homogenization was performed in a hydrogen atmosphere with a dew point of ~70 °C for 1.5 h.

The electrochemical etching step through the epitaxial layer was controlled on the basis of the current-voltage characteristics of the electrolyte-semiconductor barrier using an Accent PN4300PC profilometer. An aqueous solution of 0.2 M ethylenediamine (Sigma Aldrich, 98 %) was used as an electrolyte in electrochemical capacitance-voltage (ECV) profiling. The structural and electrical properties of the obtained epitaxial structures were studied using an X Pert PRO MRD XL diffractometer in a single-crystal mode.

3. RESULTS AND DISCUSSION

Since LT-GaAs used in device structures has a thickness of several microns, it is important to use a technique with high resolution to study its galvanomagnetic parameters. These include precision C-V profilometry. Fig. 1 shows the profiles of the distribution of the concentration of charge carriers on the thickness of the layers crystallized at the same temperature and time regimes. Each of the four studied samples was grown from gallium melts, which differed in the concentration of ytterbium and aluminum added to them.

![Graph](image)

**Fig. 1** – Profiles of charge carrier distribution in the epitaxial layers of GaAs obtained from gallium melts doped with ytterbium and aluminum: 1 – 3·10⁻³ at. %; 2 – 3·2·10⁻³ at. %; 3 – 3·5·10⁻³ at. %; 4 – 4·2·10⁻³ at. %; (1-4) Al: 1·10⁻³ at. %.

All test samples were crystallized from melt-gallium solutions doped with the same amount of aluminum (1·10⁻³ at. %), which was chosen in such a way that the band gap of the semiconductor did not change, or its change was minimal and did not exceed 0.1 eV. In this case, we can assume that the layer will have the properties of a binary compound GaAs, not a solid solution. The concentration of ytterbium in the melts from which samples 1-3 crystallized increased from 3·0·10⁻³ at. % to 3·5·10⁻³ at. %, which caused a decrease in the concentration of electrons from ~1·10⁻¹⁶ cm⁻³ to ~1·10⁻¹⁵ cm⁻³ (Fig. 1, curve 1-3). The type of profiles does not change significantly. The distribution of the electron concentration over the thickness of GaAs layers is quite homogeneous. Increasing the amount of ytterbium in the melt to 4·2·10⁻³ at. % significantly changes the electron concentration distribution profile (Fig. 1, curve 4). The electron concentration decreases to ~2·10⁻¹⁵ cm⁻³ and there is a change in the type of conductivity of the layer from n-type to p-type.

A p-n junction is formed on the surface of the n-type substrate. The p-GaAs layer is characterized by a homogeneous thickness distribution of holes.

The results obtained here on the nature of the behavior of the concentration of charge carriers from the concentration of REE in the gallium melt completely coincide with the picture we obtained in [6] using the Hall effect method, which gave the average values of concentrations in the epitaxial layers.

The most probable mechanism of the combined effect of ytterbium and aluminum in the formation of charge distribution profiles in the samples obtained in all experiments is the interaction of REE ytterbium with oxygen and background impurities (mostly donors) [5]. Aluminum, in addition to enhancing the generating action of ytterbium, significantly affects the redistribution of background impurities (especially amphoteric) on the sublattices of gallium arsenide occupying vacancies in the gallium sublattice [7]. As known, with complex alloying, a change in the concentration of electrons is accompanied by an increase in their friability right up to the point of inversion of the type of conductivity.

Further increase in the amount of REE in the melt due to the higher critical concentrations can lead to an increase in the photoluminescent and structural properties of layers. This confirms the results of the study of the structural perfection of the samples No. 1-4 with the HRD methodology, which are given in Table 1 and Fig. 2. Samples No 1 and No 2 are the most successful. The half-widths of sample No 3 (Table 1) slightly increase, while the intensity at the peak decreases, which may indicate some deterioration in the structural perfection of sample No 3. The peak intensity of sample No 4 barely reaches 300 thousand in comparison with other samples.

**Table 1** – Half-width scans and their peak intensities

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Half-width omega-2 theta scan (s) and peak intensity (imp/s)</th>
<th>Half-width omega scan (s) and peak intensity (imp/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No 1</td>
<td>17.4 913570</td>
<td>17.7 835605</td>
</tr>
<tr>
<td>No 2</td>
<td>17.2 862110</td>
<td>19.3 826150</td>
</tr>
<tr>
<td>No 3</td>
<td>17.5 828785</td>
<td>19.7 821035</td>
</tr>
<tr>
<td>No 4</td>
<td>16.1 269142</td>
<td>65.8 295503</td>
</tr>
</tbody>
</table>

The half-width of the omega scan is 65.8 s, which is quite a lot and may indicate the formation of a significant number of defects.

Therefore, based on the above results, it can be argued that at certain optimal concentrations of ytterbium (3.0-3.2)·10⁻³ at. % and aluminum 1·10⁻³ at. %, it is possible to receive structurally perfect GaAs epitaxial layers with a low concentration of carriers or to obtain layers with a significant concentration of defects at high concentrations of ytterbium in the melt.
Analyzing the obtained profiles of the charge carrier distribution (Fig. 1), we can see that the thicknesses of the transition layers are \( \approx 0.4-0.5 \) microns. If an active layer of the instrumental epitaxial structure has a thickness of about 1 micron, then the transition layer can already significantly affect its galvanomagnetic properties. So, it makes sense to reduce its thickness.

Shown in Fig. 1 and Fig. 2, the results obtained using high-resolution C-V profilometry and HRD make it possible to assess the nature of the charge carrier distribution along the layer thickness and determine the thickness of the transition layers, and thus adjust the crystallization modes so as to obtain layers with the desired parameters. Fig. 3 and Fig. 4 show the distribution profiles of the two epitaxial layers obtained under different technological modes. Technological modes of crystallization of both layers, the electron concentration distribution profiles of which are shown in Fig. 3 and Fig. 4, differ only in the rates of temperature decrease. The first sample (Fig. 3, curve 1) was obtained at a rate of temperature decrease of 1.5 °C/min, and the second one (Fig. 4, curve 2) – at a rate of temperature decrease of 0.3 °C/min.

From the comparison of the nature of the charge carrier distribution at the interface between the epitaxial substrate layer of both samples, we see that the interface of the second sample is sharper. Consider in more detail the mechanism of formation of transition layers under such technological conditions. During the homogenization of the melt solution throughout its volume, there is a homogeneous distribution of all chemical elements, including uncontrolled impurities. After homogenization and contact with the substrate, the melt solution is cooled at a controlled rate.

In the process of crystallization of the GaAs layer, all controlled and uncontrolled impurities in the gallium melt solution can be incorporated into the epitaxial layer, and their amount in the solid phase will be determined by segregation coefficients. We also added ytterbium and aluminum to the gallium melt, the role of which is to significantly reduce the number of uncontrolled impurities that can get into the epitaxial layer. A feature of REE is their high chemical activity against oxygen and most donor uncontrolled impurities, which is manifested in the formation of the corresponding chemical compounds with these impurities. These chemical compounds have large molecule sizes and are usually electroneutral, so they cannot be incorporated into the crystal lattice of the epitaxial layer of gallium arsenide that crystallizes. Obvious that the probability of interaction of REE with background impurities will depend on the ratio of their concentrations in the melt. For effective interaction, the concentration of ytterbium in the melt must be at least of the same order or greater than the concentration of uncontrolled impurities.

The estimated concentration of uncontrolled donors that may enter the epitaxial layers may reach \( N^{\text{Don}} + N^{\text{Acceptor}} \approx 2 \times 10^{17} \text{ cm}^{-3} \) [6], which is quite a significant value, and the concentration of typical acceptor impurities is \( \approx 1.2 \times 10^{16} \text{ cm}^{-3} \) [6]. The concentration of ytterbium in the gallium melt used in our experiments is about \( (3-9) \times 10^{15} \text{ cm}^{-3} \), which is commensurate with the concentration of uncontrolled impurities in the melt, given their segregation coefficients.

Therefore, we can assume that under such conditions the effective interaction of ytterbium with uncontrolled impurities in the melt solution is ensured.

It is clear that such interaction with uncontrolled impurities occurs with the same probability in the entire volume of the melt, so epitaxial layers are formed with a homogeneous distribution of electrons in the thickness of the layer. This is also facilitated by the constant value of the crystallization rate of the layer.
Crystallization occurs somewhat differently at the initial moment after contact of the gallium solution-melt with the substrate. In the low-temperature version, liquid-phase epitaxy is used, usually supersaturated by 5-10 °C on arsenic solution-melt of gallium to ensure high-quality surface morphology. When the supersaturated melt is in contact with the substrate at the initial moment, the rate of crystallization of the layer is much higher than in the case of using a saturated melt [8]. Gradually, in the process of growth, the amount of supersaturation decreases, and we approach the equilibrium conditions of crystallization.

At low epitaxy temperatures, the transition process lasts 30-60 s, and during this time a transition layer of a certain thickness can be formed. If crystallization of the layer occurs at high rates of temperature decrease, the process of introduction of impurities from the melt into the solid phase is somewhat different. The effective segregation coefficient of impurities plays a decisive role in this process:

\[ k_{\text{eff}} = \frac{k_i}{k_i + (1-k_i)\exp(-\left(V_{\text{cry}} \cdot \delta/\Delta V\right)} \]  

(1)

where \( k_{\text{eff}} \) is the effective impurity distribution coefficient (effective segregation coefficient); \( k_0 \) is the equilibrium impurity distribution coefficient; \( V_{\text{cry}} \) is the crystallization rate, microns/s; \( \delta \) is the thickness of the diffusion layer, microns; \( \Delta V \) is the diffusion coefficient of the impurity in the liquid phase, microns²/s.

As can be seen from (1), the effective segregation coefficient of the impurity under the conditions of technological processes in the same temperature range and the use of the same solvent (same values of \( \delta \) and \( \Delta V \)) depends only on the crystallization rate, which is an argument in the exponential dependence, affecting the value of the effective coefficient of segregation of impurities. According to this effect, reducing the rate of temperature decrease during crystallization will reduce the crystallization rate and, according to formula (1), reduce the effective segregation coefficient of background impurities, and, thus, lead to a short-term increase in the background impurity concentration and an increase in the probability of interaction of these impurities with ytterbium. The consequence of these processes will be a reduction in the number of uncontrolled impurities that enter the epitaxial layer that will lead to the formation of a sharper interface.

4. CONCLUSIONS

Therefore, based on the above results, it can be stated that at certain optimal concentrations of ytterbium (3.0-3.2) \( 10^{-3} \) at. % and aluminum 1 \( 10^{-3} \) at. %, it is possible to obtain structurally perfect GaAs epitaxial layers with low carrier concentration, or to obtain layers with a significant concentration of defects at high concentrations of ytterbium in the melt. Each of these types of layers has its application in the corresponding device structures.

The use in the technological process of crystallization of the n-GaAs-n+GaAs structure complex doping of gallium melt with ytterbium and aluminum and modulation of the rate of temperature decrease allows to obtain a sharper interface.

The main factors causing this effect are the dependence of the segregation coefficients of alloying and uncontrolled impurities on the rate of crystallization and their heteration in the gallium solution-melt of ytterbium and aluminum.

REFERENCES

GaAs з низькою концентрацією носіїв, а модуляція швидкості зниження температури дозволяє отрима-ти більш різку границю розділу шарів з різним рівнем легування. Такі шари можна використовувати в складі фотодіодних чи НВЧ структур. Встановлено, що збільшення концентрації ієрбію в розплаві спричиняє погіршення структурних властивостей шарів, зумовлене генерацією додаткових дефектів, що може бути використано для створення оптоелектронних пристроїв терагерцового діапазону.

Ключові слова: Арсенід галію, Рідкоземельний елемент, Профіль розподілу носіїв заряду, Інтерфейс, Приклади терагерцового діапазону.