

# Crystallization of low-temperature gallium arsenide for device structures in the terahertz range

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## Introduction

Low-temperature gallium arsenide (LT-GaAs), also known as low-temperature grown GaAs, can serve various purposes in the fabrication of epitaxial device configurations. It finds utility as an active layer in devices like Gunn diodes, terahertz devices, and thin-film solar cells. However, its characteristics can substantially differ or even clash across these device categories.

For instance, semiconductor-based photoconductive antennas with short-lived nonequilibrium charge carriers (typically lasting picoseconds or less) are employed for generating and detecting terahertz radiation. The feasibility of this hinges on LT-GaAs having a notable presence of structural point defects or imperfections in the form of deep centers. In LT-GaAs, the density of these defects can be roughly around  $10^{20} \text{ cm}^{-3}$ . Elevating their concentration can lead to enhanced performance of optoelectronic devices in the terahertz range.

Conversely, in the context of Gunn diodes or p-i-n photodiode structures, the active layer necessitates low carrier density and, crucially, high carrier mobility. This attribute is feasible only in nearly defect-free layers possessing minimal defects of diverse origins.

Hence, the exploration of a universal technical strategy to tackle such divergent challenges becomes intriguing. One such approach involves the utilization of complex contemporary doping with rare earth elements (REE) and isovalent impurities (IVI) during the low-temperature liquid-phase epitaxy (LT LPE) growth process. Essential conditions for this approach encompass: 1. Attaining low crystallization rates akin to those achieved through methods like molecular-beam epitaxy (MBE) and metalorganic vapor-phase epitaxy (MOVPE) at reduced pressures; 2. Recognizing that liquid-phase epitaxy for  $\text{A}_3\text{B}_5$  materials is uniquely suited for fully harnessing the benefits of rare-earth element doping, with a primary advantage being the controlled manipulation of the defective-impurity structure of semiconductors. Unlike other techniques where rare-earth elements contribute uncontrolled impurities within the semiconductor matrix, the majority of these impurities remain as REE compounds in the melt solution in the case of REE doping. Only a limited quantity of REE atoms infiltrate the REE crystal lattice, functioning as heteroepitaxial centers.

This study aims to scrutinize the impact of complex doping involving REE and IVI on the electrophysical properties and structural integrity of epitaxial LT-GaAs layers. These layers are generated via LT LPE, and the investigation is conducted with an eye towards their potential incorporation into diverse microelectronic device configurations.

## Investigation of carrier concentration across the layer thickness

Given that LT-GaAs, utilized in device configurations, exhibits a thickness spanning multiple microns, the employment of a high-resolution technique becomes imperative for investigating its galvanomagnetic properties. Precision C-V profilometry proves valuable in this regard. Figure 1 illustrates the profiles detailing the distribution of charge carrier concentration across the layer thickness, which were crystallized under the same temperature and time conditions. All four samples under scrutiny were grown from gallium melts, each distinct in the content of ytterbium and aluminum introduced. All test specimens were solidified from gallium solution-melts doped with a consistent amount of aluminum ( $1 \cdot 10^{-3}$  at %). This selection was made to ensure minimal alteration, within 0.1 eV, in the semiconductor's band gap width, implying that the layer would largely exhibit GaAs binary compound characteristics rather than those of a solid solution. The ytterbium concentration in the melts used for samples 1-3 progressively increased from  $3.0 \cdot 10^{-3}$  at % to  $3.5 \cdot 10^{-3}$  at %, consequently causing a decrease in electron concentration from  $\approx 1 \cdot 10^{16} \text{ cm}^{-3}$  to  $\approx 1 \cdot 10^{15} \text{ cm}^{-3}$  (Fig.1 curves 1-3). The profiles' nature remains relatively consistent. The distribution of electron concentration through the GaAs layers remains notably uniform. A more substantial increase in ytterbium quantity to  $4.2 \cdot 10^{-3}$  at % within the melt notably alters the electron concentration distribution profile (Fig.1 curve 4). The electron concentration drops to  $\approx 2 \cdot 10^{15} \text{ cm}^{-3}$ , leading to a shift in layer conductivity type from n-type to p-type. Resultantly, a p-n junction forms on the surface of the n-type substrate, with the p-GaAs layer featuring a uniformly distributed thickness of holes. The plausible mechanism underlying the combined influence of ytterbium and aluminum on the charge distribution profiles in all experimental samples is the interaction between ytterbium and oxygen, along with background impurities (primarily donors). Additionally, aluminum, aside from enhancing ytterbium's generating effect, significantly influences the redistribution of background impurities, especially amphoteric ones, within the sublattices of gallium arsenide occupying vacancies in the gallium sublattice. Complex alloying is known to accompany changes in electron concentration, often leading to increased fragility up to the point of conductivity type inversion. Further augmentation of rare earth element content within the melt due to higher critical concentrations might elevate the photoluminescent and structural attributes of layers. This is corroborated by the outcomes of the HRD methodology analysis of samples No. 1-4 presented in Fig. 3. Samples No. 1 and No. 2 exhibit the most favorable results. Sample No. 4's peak intensity barely reaches 300 thousand, in contrast to other samples.

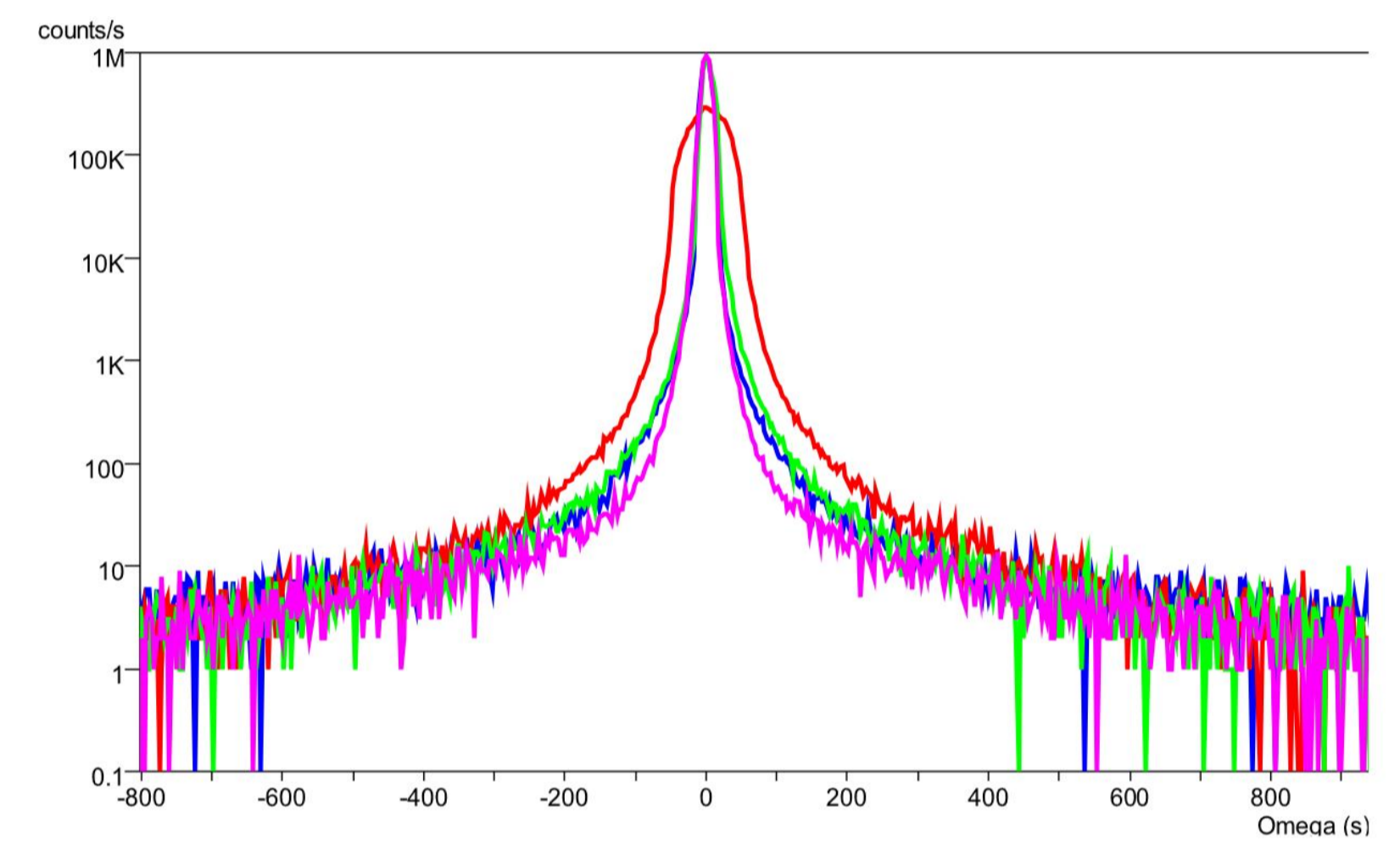


Fig.1. High resolution (TCS) omega scans of reflex (111). (sample №1 – pink curve; sample № 2 – blue curve; sample № 3 – green curve; sample № 4 – red curve).

## Profiles of charge carriers distribution

The outcomes portrayed in Figures 1 and 2, facilitated by high-resolution C-V profilometry, furnish the capability to evaluate the nature of charge carrier distribution across the layer thickness. This insight also aids in determining the thickness of transition layers, enabling the adjustment of crystallization methods to obtain layers with desired characteristics.

Figure 2 illustrates the distribution profiles of two epitaxial layers generated using distinct technological approaches. The crystallization methods for both layers, as showcased by the electron concentration distribution profiles in Figure 2, differ solely in the rates of temperature reduction. The first sample (curve 1) was produced with a temperature reduction rate of  $1.5 \text{ }^\circ\text{C}/\text{min}$ , while the second (curve 2) employed a temperature reduction rate of  $0.3 \text{ }^\circ\text{C}/\text{min}$ .

Upon comparing the nature of charge carrier distribution at the interface between the epitaxial substrate layer of both samples, it becomes evident that the interface of the second sample is more distinct. A closer examination of the mechanism responsible for transition layer formation under such technological conditions reveals that, during the homogenization of the melt solution, a uniform distribution of all chemical elements occurs, encompassing uncontrolled impurities. Following homogenization and contact with the substrate, the melt solution is subjected to controlled cooling.

In the process of crystallizing the GaAs layer, all controlled and uncontrolled impurities within the gallium melt solution can be incorporated into the epitaxial layer, with their quantity in the solid phase dictated by segregation coefficients. The ytterbium and aluminum added to the gallium melt serve to notably reduce the influx of uncontrolled impurities into the epitaxial layer, alongside their role in enhancing ytterbium's generating effect. Notably, rare earth elements, due to their elevated chemical reactivity against oxygen and numerous donor impurities, facilitate the formation of corresponding chemical compounds with these impurities. These compounds typically exhibit larger molecule sizes and possess an electroneutral character, rendering them unsuitable for incorporation into the crystallizing epitaxial layer's crystal lattice.

The process of crystallization unfolds somewhat differently at the initial moment following the contact of the gallium solution-melt with the substrate. In the low-temperature variant of liquid-phase epitaxy, a slight supersaturation of around  $5\text{-}10^\circ\text{C}$  on the arsenic solution-melt of gallium is employed to ensure optimal surface morphology. At the outset of contact, the rate of layer crystallization when the melt is supersaturated is notably higher compared to the utilization of a saturated melt. As growth progresses, the degree of supersaturation gradually diminishes, ultimately reaching equilibrium crystallization conditions. Under low-temperature epitaxy, this transitional phase lasts approximately 30-60 seconds, during which a transition layer of specific thickness is formed.

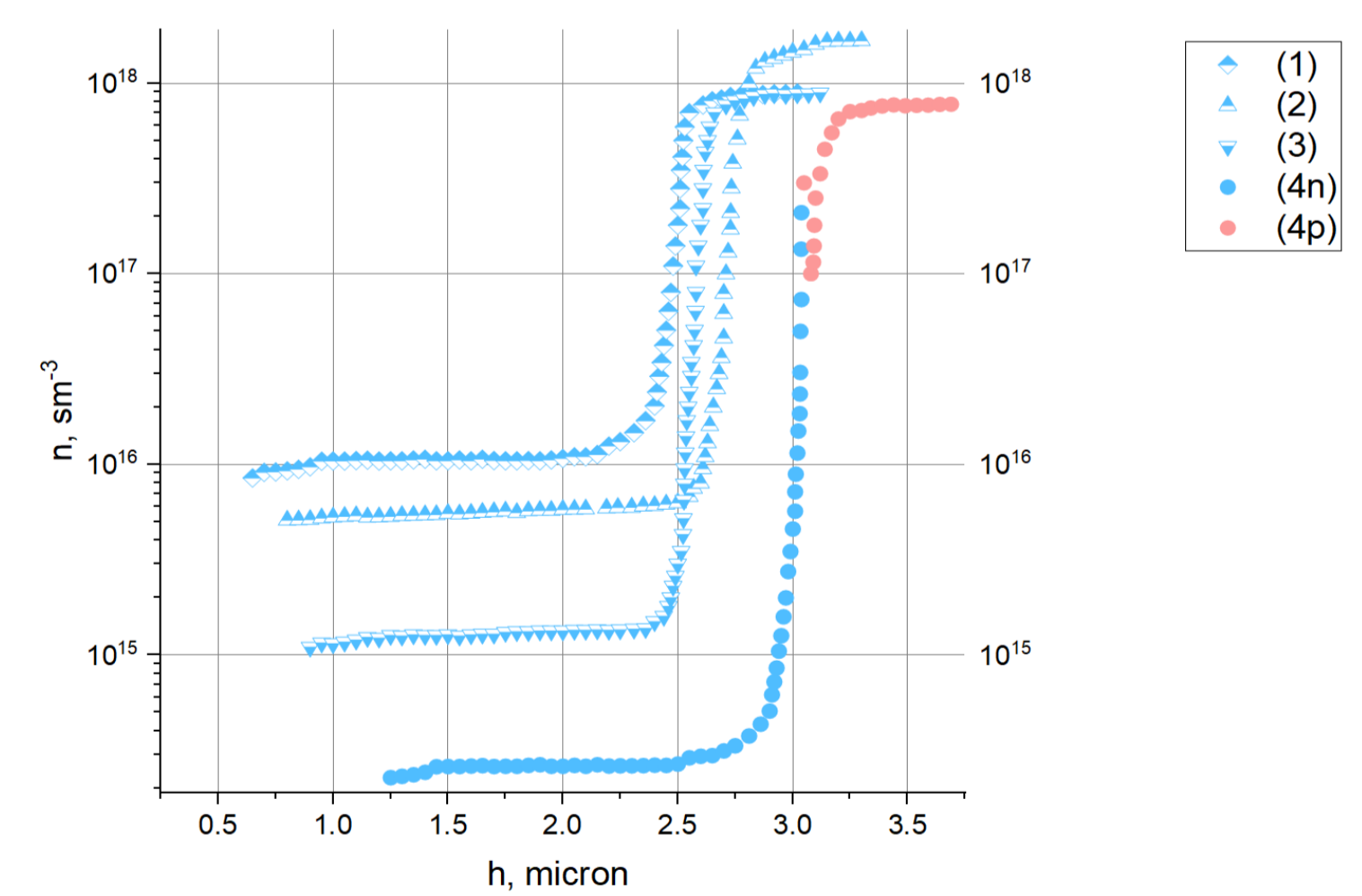


Fig.2. Profiles of charge carriers distribution in the epitaxial layers of GaAs obtained from gallium melts doped with ytterbium and aluminum: 1-  $3.0 \cdot 10^{-3}$  at %; 2-  $3.2 \cdot 10^{-3}$  at %; 3-  $3.5 \cdot 10^{-3}$  at %; 4-  $4.2 \cdot 10^{-3}$  at %. (1-4) Al:  $1.0 \cdot 10^{-3}$  at %.

## Conclusions

Consequently, based on the outcomes detailed earlier, it can be affirmed that specific optimal concentrations of ytterbium (ranging from  $3.0$  to  $3.2$ )  $\cdot 10^{-3}$  at % and aluminum at  $1 \cdot 10^{-3}$  at % offer the potential to produce structurally impeccable GaAs epitaxial layers. These layers exhibit either low carrier concentration or, alternatively, a notable concentration of defects, particularly at elevated ytterbium concentrations in the melt. Each variant of these layers finds its relevance in corresponding device configurations.

Employing complex doping of the gallium melt with ytterbium and aluminum within the technological crystallization process for the n-GaAs - n + -GaAs structure, coupled with modulation of the rate of temperature reduction, serves to yield a more pronounced interface.

This effect is principally driven by the interplay of factors like the influence of crystallization rate on the segregation coefficients of alloying and uncontrolled impurities, as well as their interaction within the ytterbium and aluminum-enriched gallium solution-melt.

