

COMPOSITION RELATED ELECTRICAL ACTIVE DEFECT STATES OF INGAAS AND GAASN

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Abstract. *This paper discusses results of electrically active defect states - deep energy level analysis in InGaAs and GaAsN undoped semiconductor structures grown for solar cell applications. Main attention is focused on composition and growth condition dependent impurities and the investigation of their possible origins. For this purpose a widely utilized spectroscopy method, Deep Level Transient Fourier Spectroscopy, was utilized. The most significant responses of each sample labelled as InG2, InG3 and NG1, NG2 were discussed in detail and confirmed by simulations and literature data. The presence of a possible dual conduction type and dual state defect complex, dependent on the In/N composition, is reported. Beneficial characteristics of specific indium and nitrogen concentrations capable of eliminating or reducing certain point defects and dislocations are stated.*

Keywords

Deep energy levels, Deep Level Transient Fourier Spectroscopy, electrically active defects, GaAsN, indium, InGaAs, nitrogen, solar cells.

1. Introduction

Optimization of fabrication processes for achieving high quality semiconductor materials is one of the most important factors in the technical advancement of semiconductor structures. Concentrated effort is focused on the achievement of perfect crystal structures, although it is very hard to maintain and define specific growth conditions. Different growth parameters can

affect the formation of defect states, such as temperature, pressure and high purity, and these can highly affect the function and electrical properties of final devices. From the energetic point of view, electrically active trap states, also called deep energy levels, are allowed states in the band gap of the semiconductor material, capable of capturing or emitting charge carriers, thereby directly influencing generation and recombination processes usually with non-beneficial effects.

In order to identify inadequacies of growth technologies, the manufacture of high quality semiconductor materials has to be supported by appropriate diagnostic approaches, in which Deep Level Transient Fourier Spectroscopy (DLTFS) has a key role [1] and [2]. Dilute-nitride InGaAsN based solar cells lattice matched to GaAs are continuously studied to realize higher efficiencies [3]. Using various indium and nitrogen concentrations in semiconductor layers, different band gaps can be achieved, suitable also for tandem solar cell applications [4].

Since a proper indium and nitrogen composition is the key element of these structures, the investigation of related deep energy levels is indispensable. In order to identify and state origins of indium or nitrogen generated deep energy levels and their behaviour at various compositions, it is essential to analyse InGaAs and GaAsN referent structures with various compositions.

The aim of this study is to assess and discuss findings from investigations of four $\text{In}_y\text{Ga}_{1-y}\text{As}$ structures with varied indium concentrations from 3.4 to 12.8 %, and five $\text{GaAs}_{1-x}\text{N}_x$ samples with various nitrogen contents from 0.9 to 1.85 %, and according to these results to report most appropriate structures with lowest defect activities.

2. Experiment

The experimental part of this study was realised based on DLTFs measurements and evaluation procedures. This method is capable of measuring and processing a set of capacitance transient signals induced by charge carrier emission or capture for a set temperature range (85–550 K). Capacitance transient signals are then processed by Fourier transformation and calculated as DLTFs spectrums. The charge carrier emission or capture is ensured by electrical excitation, meaning different biased states of the examined structure applying reverse V_R and so called filling voltage V_P conditions. For a given time period T_W the transient signal changes exponentially and outlines a peak in the DLTFs spectrum. Each peak is a direct result of a possible defect state or defect complexes.

Advantages of this method like precision, high sensitivity and adaptability ensures accurate trap parameter outputs (activation energy ΔE_T , capture cross section σ_T and trap concentration N_T), calculated by Arrhenius curves - temperature dependence of the emission rate [1] and [2]. The accuracy of the method is mainly affected by complex situations when different defect complexes are interacting, which results in multi-level responses and complicated broad spectra. In such cases different evaluation approaches or mathematical deconvolution and simulation processes are used and compared by literature data.

2.1. Indium Related Defect States of InGaAs

Four InGaAs structures with variable indium compositions were investigated. All these samples were grown at the Wroclaw University of Science and Technology by Atmospheric Metal Organic Vapour Phase Epitaxy. As Tab. 1 lists the indium content was varied from 3.4 to 12.8 % by different flow rates of the indium dopant source trimethylindium (V_{TMIn}) [5]. Common flow rates of trimethylgallium (V_{TMGa}) and arsine (V_{ASH3}) were set to 7 and 50 ml·min⁻¹. Each InGaAs layer was deposited on a GaAs 450 nm buffer layer and n-GaAs:Si $n = \frac{1}{2 \cdot 10^{18}} \text{ cm}^{-3}$ substrate. Structural properties were identical, only differences in layer widths and composition were observed at varied V_{TMIn} flow rates (Tab. 1). DLTFs investigation of such referent structures is quite interesting, since we are able to monitor and analyse the behaviour of electrically active defect states at different band gaps resulted from the In content. Deviation of activation energies is not unusual, meaning that not only slightly shifted DLTFs peaks but also fluctuating activation energies are assumed.

As Fig. 1 shows this prediction was confirmed by the DLTFs spectra comparison of each sample measured at

same experimental conditions, where to clarify the investigation process group labels were introduced. If we closely examine e.g. the InG2 group (Fig. 1), we see that at this temperature range (300 K to 360 K) a positive peak was outlined in all cases but with shifted peak positions. We have assumed that these responses are originating from identical deep energy levels but significant at slightly different temperatures caused by the band gap difference [6]. Standard evaluation procedure resulted activation energies in range from 0.46 eV to 0.48 eV, hence similar values in each case. All the observed defect states were evaluated in a similar manner (InG1 - InG3).

Tab. 1: Distinct composition and structural parameters of the investigated GaAsN samples.

Structure	H_2 through V_{TMIn} (ml·min ⁻¹)	$i \text{ In}_y \text{ Ga}_{1-y} \text{ As}$	
		(nm)	y (%)
InGaAs i I	5	~ 110	3.4
InGaAs i II	20	~ 110	8.9
InGaAs i III	32	~ 120	10.5
InGaAs i IV	35	~ 110	12.8

By means of trap concentrations (peak amplitude) it is hard to conclude a definitive correspondence. Peak amplitudes are directly influenced by defect concentrations, locally distributed defects, and the investigated sample's contact area. Contact areas were more or less equal, although minor changes due to unevenly prepared contacts were expected, however, the number of significant trap states, eliminated or generated, can give a hint about the most pure sample and the proper indium content.

The DLTFs investigation indicates the following statements (see Fig. 1 and Tab. 2):

- higher indium content above 8.9 % reduces or entirely suppresses low temperature (below 250 K) point defects [7],
- two significant defect states or complexes were identified present in all samples (InG2 and InG3),
- InG2 was identified as a Cu (~0.48 eV) related hole trap [8] and [9],
- InG3 was evaluated as a probable dual state complex EL2 (~0.77 eV) and its meta stable double donor state EL2²⁺ (~0.57 eV) [8] and [9].

Tab. 2: Deep energy level parameters of the investigated GaAsN samples.

Trap	peak	$\Delta E_{Tn,p}$ (eV)	$\sigma_{n,p}$ (cm ²)
ING1	positive	~0.25	~5.23·10 ⁻¹⁸
	negative	~0.34	~2.29·10 ⁻¹⁶
ING2	positive	~0.48	~3.3·10 ⁻¹⁷
ING3	positive	~0.57	~2.0·10 ⁻¹⁴
	negative	~0.77	~1.9·10 ⁻¹⁷

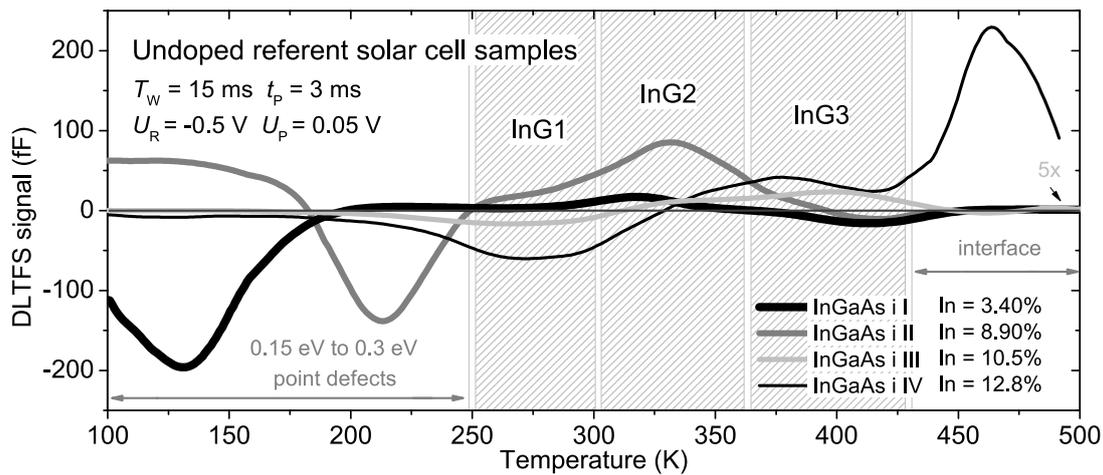


Fig. 1: DLTFs spectra of InGaAs undoped referent samples at different In concentrations, measured at identical experimental conditions.

These findings indicated that there is a high possibility that the observed formation of the identified EL2 and its meta-stable state is connected to the In concentration. A clear transition occurred around 9 to 10 % and was experimentally supported by the examined DLTFs results (Fig. 1 InG3 changing peak from negative to positive). The EL2 dominant native deep donor in GaAs is one of many intrinsic trap states investigated in III-V semiconducting compounds. It can be transformed to a meta-stable state e.g. by illumination of the crystal at low temperatures. It is not entirely understood what introduced this defect complex in the investigated samples, therefore further investigations are needed to fully evidence a possible In content relation.

At the analysed experimental conditions only samples InGaAs i I and II showed significant trap levels at lower (point defects) and InGaAs IV at higher temperatures (interface states).

Sample InGaAs i III with indium 10.5 % should be considered as the one with the lowest defect activity, where lowest peak amplitudes were observed, five times multiplied for spectral comparison.

The most unstable sample by these results was InGaAs IV with the highest In content, since it showed DLTFs peaks in the whole 200 K to 500 K range.

2.2. Nitrogen Related Defect States of GaAsN

The GaAsN DLTFs investigation included five referent samples with various nitrogen concentrations, addressing not only composition but also growth condition dependence of electrically active defect states. Each structure was prepared at different growth temperatures (585 °C, 605 °C, 595 °C, 565 °C and 575 °C)

to achieve a mixture of the nitrogen concentration. The following parameters were applied: growth precursor tertiarybutylhydrazine (V_{TBHy}) at flow rate of $1500 \text{ ml}\cdot\text{min}^{-1}$, trimethylgallium $V_{TMGa} = 7 \text{ ml}\cdot\text{min}^{-1}$ and arsine $V_{ASH3} = 50 \text{ ml}\cdot\text{min}^{-1}$. Each GaAsN layer was deposited on a GaAs 450 nm thick buffer layer and n-GaAs:Si $n = \frac{1}{2\cdot 10^{18}} \text{ cm}^{-3}$ substrate. Table 2 lists the main differences in composition and structural properties. This fabrication factor is also favourable for increasing or decreasing defect tendencies. Once again, shifting DLTFs curves had to be considered and group levels investigated (Fig. 2 NG1 and NG2) due to band gap differences.

As Fig. 2 shows, a broad peak with high trap concentration of sample GaAsN I (lowest N) was obviously dominating the spectrum comparison. Deep energy levels NG1 and NG2 were present in all samples, while this broad peak was only significant for this sample. It was assumed that higher nitrogen concentrations and/or temperature growth are capable of reducing/eliminating dislocation defects [10]. This reduction probably occurs at $N = 1 \%$ and is maintained at higher concentrations as well. Defect levels NG1 and NG2 were more relevant for these samples, although there was no exact correlation found between DLTFs amplitudes and the N concentration and growth temperature parameter pair. In overall view we can conclude that the DLTFs peaks were highest in two cases: for the sample GaAsN II with the highest growth temperature of 605 °C and concentration $N = 1.15 \%$, and for GaAsN V with the highest nitrogen content $N = 1.85 \%$ and growth temperature of 575 °C (Fig. 2).

It could be speculated that both temperature and the nitrogen content tends to increase the defect concentration. Possible explanation on this behaviour is a complex defect, which could include a nitrogen induced defect state, increasing the signal at higher

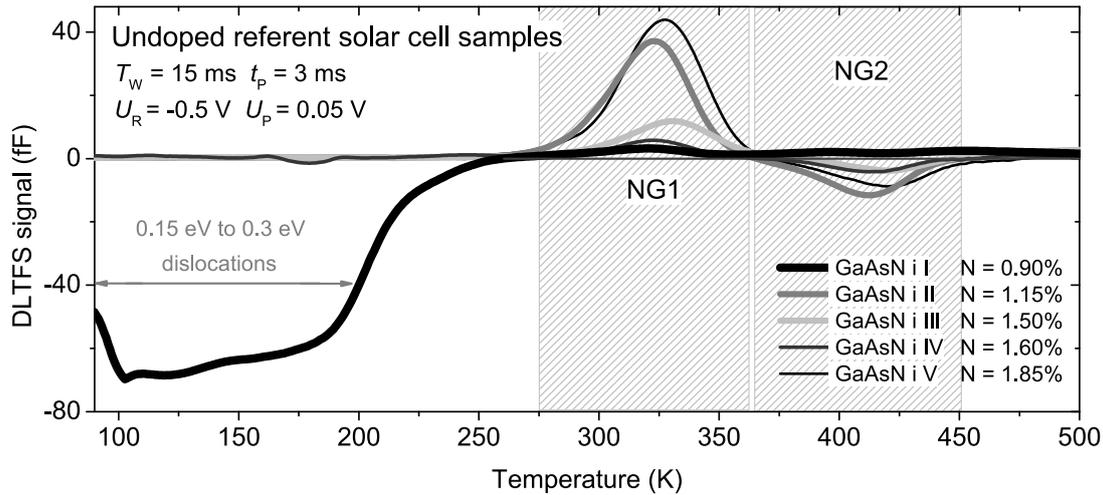


Fig. 2: DLTFS spectra of GaAsN undoped referent samples at different N concentrations, measured at identical experimental conditions.

Tab. 3: Distinct composition and structural parameters of the investigated GaAsN samples.

Structure	Growth temp. T_g (°C)	GaAs _{1-x} N _x	
		(nm)	x (%)
GaAsN I	585	~65	0.90
GaAsN II	605	~100	1.15
GaAsN III	595	~126	1.50
GaAsN IV	565	~100	1.60
GaAsN V	575	~130	1.85

nitrogen concentrations, co-existing with a GaAs defect becoming more dominant at higher temperatures (Tab. 4).

Tab. 4: Deep energy level parameters of the investigated GaAsN samples.

Trap	peak	$\Delta E_{Tn,p}$ (eV)	$\sigma_{n,p}$ (cm ²)
ING1	positive	~0.48	~1.7·10 ⁻¹⁷
	negative	~0.54	~3.9·10 ⁻¹⁶
ING2	positive	~0.71	~8.0·10 ⁻¹⁶
	negative	~0.66	~5.5·10 ⁻¹⁶

This condition may be described for defect groups NG1 and NG2 as well, since NG1 was identified as a complex of a Cu related GaAs trap (NG1* \cong 0.46 eV) together with a nitrogen induced defect (NG1** \cong 0.54 eV) [11]. Cu was confirmed in InGaAs samples as well, strongly indicating that this assumption is correct. The NG2 interpretation is more complex since the spectrum transition occurred once again (see Fig. 2 NG2). In this case it was identified as a dual type complex (two different defect state responses as a complex spectrum) rather than a dual state as for InGaAs.

More precisely, as a possible nitrogen related negative signal (NG2 \cong 0.66 eV) with a GaAs assumed positive one (NG2 \cong 0.71 eV) [12]. Since the positive signal of NG2 at the investigated DLTFS measurement

conditions was only visible in GaAsN I (0.9 % of nitrogen, at growth temperature of 585 °C), it can be concluded that the growth temperature of 585 °C induces the most dominant state of the GaAs defect.

GaAsN IV with 1.60 % growth at 565 °C could be considered as the most balanced structure where NG1 and NG2 were the lowest and at the same time dislocations were suppressed. In means of N related defect concentration reduction, lower nitrogen content should be more relevant. An optimized growth temperature should be proposed avoiding the generation of growth temperature sensitive GaAs defects, but efficient enough to ensure a suitable nitrogen concentration eliminating dislocations. Since these disappeared already at 1.15 %, N content around this value should be considered with growth temperature lower than 585 °C. For these parameters the positive NG2 signal is probably dominant.

3. Conclusion

The reported comprehensive InGaAs and GaAsN DLTFS investigation showed that each referent structure can be a source of several defects. Fundamental findings were observed related to composition and possible growth condition dependent defect states. New knowledge was acquired about emission and capture processes connected to indium and nitrogen, important to support the InGaAsN research and application in solar cells. According to the reported electrically active defect behavior, the InGaAs sample with 10.5 % can be stated as the most appropriate, since low temperature point defects were eliminated and trap concentrations were low. GaAsN referent structures showed several dislocations at low temperatures disappearing around

1 % of nitrogen, nevertheless, the growth of the structure with 1.6 % and 565 °C suppressing dislocations and reducing GaAs/N complex defect amplitudes can be stated as the most balanced one. Moreover, growth temperatures lower than 585 °C are arguable, at which significant trap states were reduced.

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