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New method of MOVPE process design for the growth of FGM AlGaAs/GaAs photodetectors

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In this paper, the authors present a new attempt to the growth of AlGaAs structures with continuous change of aluminum content by metalorganic vapor phase epitaxy (MOVPE) technique. The new method of design of multistage growth process for functionally graded semiconductor materials (FGM) has been proposed. A comparison between classical single stage and multistage growth process has been carried out. The analysis of PVS, ECV and SIMS results of fabricated photodetector structures shows significant differences in composition profile of theoretically estimated and fabricated structures, and prove that the new conception of multistage process has more advantages over classical single stage procedure.

Keywords: growth models, metalorganic vapor phase epitaxy (MOVPE), gallium compounds, semiconducting III-V materials.

1. Introduction

Due to their unique properties, semiconductor heterojunctions with wide transitional regions are widely applied in nano- and microcrostructures. FGMs, as they are called (functionally graded materials), were originally applied in metallurgy and material engineering [1–3], but over the last years have become more and more popular in semiconductor technology [4–9]. The continuous gradation of alloy composition allows us to achieve superior optical, electrical and mechanical properties of the devices, compared to their classical non-graded equivalent.

Controlling the MOVPE process conditions poses a serious challenge because of a large number of parameters which are to be appropriately set and maintained unchanged during each process stage. Another complex issue is the repeatability of

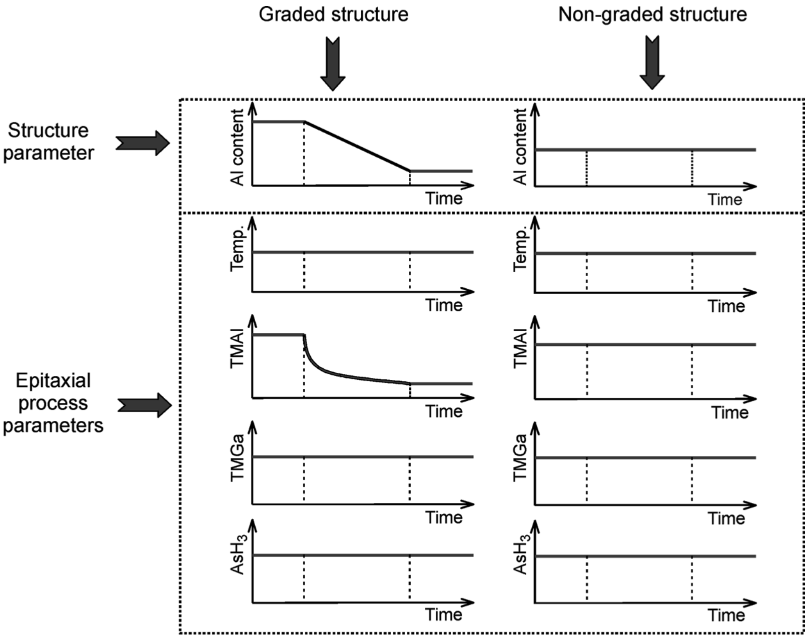

Fig. 1. Comparison between homogenous and graded layer growth approaches.

the parameters of particular process run. All those factors strongly influence the electrical and optical properties of grown structures. The main goal of our work (some early results were presented in [10, 11]) was to investigate the possibility of shaping spectral response of AlGaAs/GaAs photodetector structures by modifying the parameters of their active graded layer. We have investigated the influence of the conditions of epitaxial process on the properties of graded layer, such as resultant profile of composition and doping. The main problem is that the composition of the layer and their growth rate do not depend linearly on the growth temperature and flow rates of chemical reactant. That is why the standard approach is not sufficient. The comparison of both approaches, for homogenous and graded layer, is schematically shown in Fig. 1. We have proposed the application of dynamic calibration procedure instead of static calibration of MOVPE process.

2. Experimental results

The growth experiments were carried out at an atmospheric pressure MOVPE system equipped with AX200R&D reactor. The (100)-oriented GaAs substrates were applied. The total carrier gas flow of H_2 was 10 l/min. Group-V source was 10% AsH_3 diluted with hydrogen and group-III sources were trimethylaluminum (TMAl) and trimethylgallium (TMGa). Silane (SiH_4) and dietylzinc (DEZn) were used as *n*- and *p*-type dopants, respectively. The growth process was performed in the range of temperatures 700−740 °C, which provide superior structural, electrical and optical quality of

$Al_xGa_{1-x}As$ epitaxial layers. The Al content in the range 0%–43% in $Al_xGa_{1-x}As$ layers was changed by altering the ratio of H_2 carrier gas that had flown through TMAl bubbler in the range 0–7 ml/min at a constant flow of H_2 gas through TMGa bubbler (10 ml/min). AsH_3 flow rate was set at a constant level of 350 ml/min. Because of the strong dependence between Al incorporation velocity and doping effectiveness, the ratio of carrier gas that had flown through DEZn bubbler was changed according to the total flow of TMAl.

2.1. Single stage process design conception

Primary experiments were carried out to check the opportunity of epitaxial deposition of functionally graded $Al_xGa_{1-x}As$/GaAs structures in a single stage MOVPE process. After theoretical consideration and computer simulation of the various FGM photodetector structures, a *p-n* junction photodetector with compositionally graded active area was proposed (Fig. 2). Based on earlier experiments and calibration curves

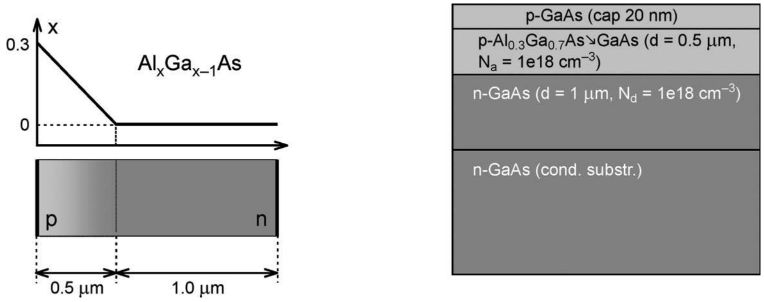

Fig. 2. Scheme of proposed *p-n* photodetector structure with compositionally graded active region.

Table. 1. Process conditions of MOVPE deposition of *p-n* $Al_xGa_{1-x}As$/GaAs photodetector structure with compositionally graded active region (↗ and ↘ indicate an increase or decrease of the parameter value during the process stage).

Stage	Time [s]	Temp. [°C]	TMGa (H_2) [ml/min]	TMAl (H_2) [ml/min]	DEZn (H_2) [ml/min]	SiH_4 [ml/min]	AsH_3 [ml/min]
Heating	1200	840	10 (50)	50 (10)	10 (20)	10	350
Temperature stabilization	600	↘670	10 (50)	50 (10)	10 (20)	1.5	350
GaAs:Si deposition	3600	670	10 (50)	20 (10)	20 (20)	1.5	350
Flow stabilization	600	↗740	10 (50)	50↘1 (500)	20↘2 (100)	100	350
$Al_xGa_{1-x}As$:Zn deposition	6300	740	10 (50)	0↗7 (500)	30↘1.5 (100)	100	350
Flow stabilization	120	740	10 (50)	50 (10)	1.5 (100)	2	350
GaAs:Zn deposition	270	740	10 (50)	50 (10)	1.5 (100)	2	350
Cooling		↘20					

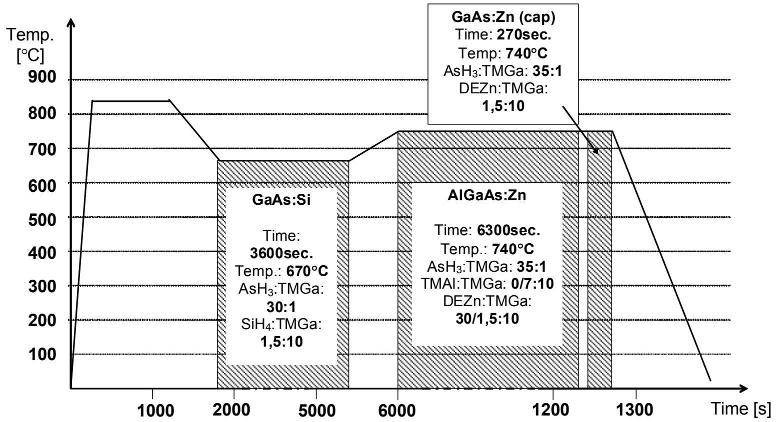

Fig. 3. Diagram of process flow of MOVPE growth of *p-n* $Al_xGa_{1-x}As/GaAs$ photodetector structure with compositionally graded active region.

of MOVPE system, the growth process of $Al_xGa_{1-x}As/GaAs$ photodetector structure was designed and carried out. MOVPE process description is schematically shown in Tab. 1 and Fig. 3 Detailed information about deposition conditions and calibration process can be found in [12].

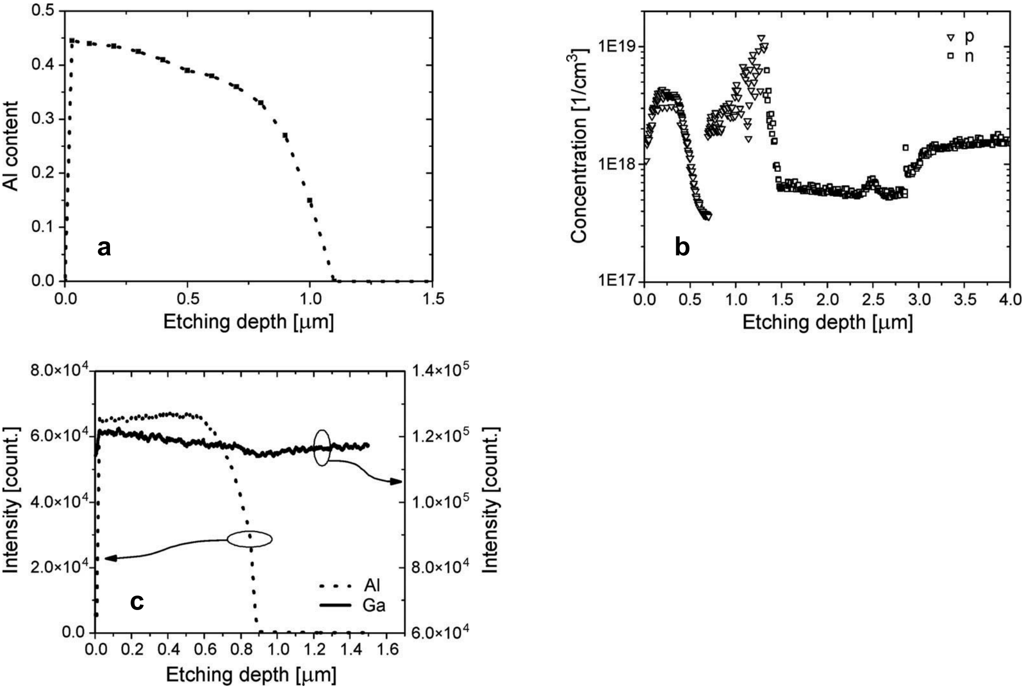

Fig. 4. PVS (**a**), ECV (**b**) and SIMS (**c**) profiles of composition and doping of compositionally graded structure of $Al_xGa_{1-x}As/GaAs$ photodetector.

A thick conductive GaAs:Si layer was deposited on GaAs:Te substrates. Next, the compositionally graded $Al_xGa_{1-x}As$:Zn layer was subsequently grown for *p-n* junction formation. Gradation of Al content in AlGaAs layer was obtained by linear altering of the ratio of H_2 carrier gas that had flown through TMAl bubbler. The H_2 flow rate was changed in the range from 0 to 7 ml/min. Simultaneously, to maintain constant incorporation level of dopants in the grown layer the flow rate of H_2 bubbling through DEZn was linearly decreased from 30 to 1.5 ml/min. Finally, a thin GaAs:Zn cap layer was deposited to prevent uncontrolled oxidation of AlGaAs layer.

Fabricated structure was structurally and electrically characterized by electrochemical capacitance–voltage (ECV) profiler (Bio-Rad PN4300) equipped with photovoltage spectroscopy (PVS) module and second ion mass spectrometer (SIMS). The profiles obtained are shown in Fig. 4.

2.2. Multistage process design conception

Because of the observed differences in the main part of compositionally graded layer (such as layer thickness, composition, doping level) between designed and fabricated epitaxial structures of *p-n* photodetectors, a new multistage process design concept has been work out. It also required performing some additional MOVPE process calibration procedures. A new concept of dynamic multistage process based on linear approximation of the main parameters of epitaxial process in finite time intervals has been proposed. In this approach, basic calibration curves (Fig. 5**a**) were used to design the epitaxial process. The new growth process of compositionally graded layer was divided into 4 (sample A) or 5 (sample B) stages in which parameters such as duration of each period of time and flow rate of carrier gas through TMGa and DEZn bubblers changed linearly. This conception is shown schematically in Figs. 5**a** and 5**b**.

The *p-n* diode structure was as follows: on (100)-oriented semi-insulated (sample B) and conductive GaAs:Si (sample A) substrates thick GaAs:Si buffer layer

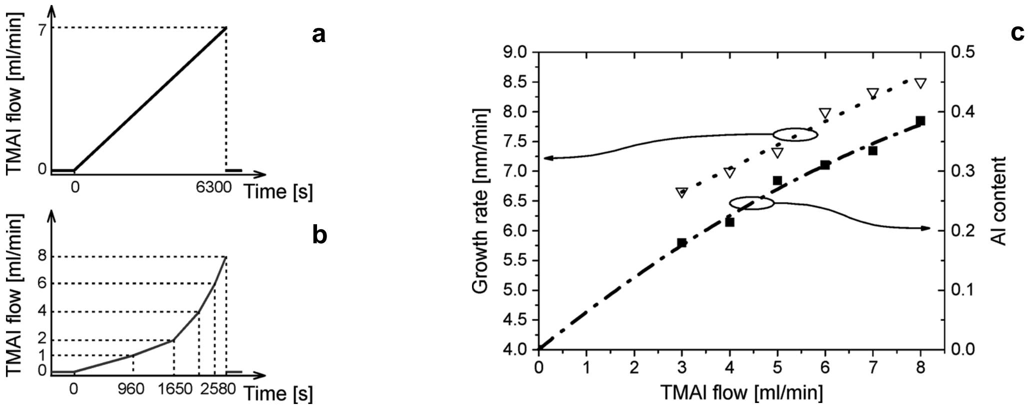

Fig. 5. Calibration curves of MOVPE system (**a**), scheme of single stage deposition of compositionally graded $Al_xGa_{1-x}As$ layer (**b**), scheme of multistage epitaxy of compositionally graded $Al_xGa_{1-x}As$ layer (sample B) (**c**).

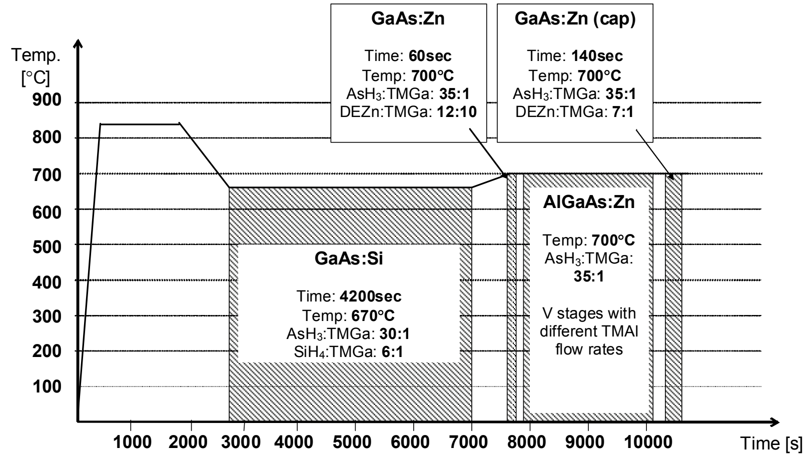

Fig. 6. Diagram of process flow of MOVPE growth of *p-n* $Al_xGa_{1-x}As/GaAs$ photodetector structure with compositionally graded active region deposited according to the multistage procedure.

T a b l e. 2. Process conditions of MOVPE deposition of *p-n* $Al_xGa_{1-x}As/GaAs$ photodetector structure with compositionally graded active region according to the multistage procedure.

	Stage	Time [s]	Temp. [°C]	TMGa (H_2) [ml/min]	TMAl (H_2) [ml/min]	DEZn (H_2) [ml/min]	SiH_4 [ml/min]	AsH_3 [ml/min]
	Heating	1800	840	10 (50)	50 (10)	10 (20)	10	350
	Temp. stabilization	600	↘670	10 (50)	50 (10)	10 (20)	1.5	350
	GaAs:Si deposition	3900	670	10 (50)	50 (10)	10 (20)	60	300
	GaAs:Si deposition	300	670	10 (50)	50 (10)	20 (100)	60	300
	Flow stabilization	600	↗700	10 (50)	10 (500)	20 (100)	100	350
	GaAs:Zn deposition	60	700	10 (50)	10 (500)	12 (100)	100	350
	Flow stabilization	120	700	10 (50)	10↘0 (500)	12 (100)	100	350
Sample A	$Al_xGa_{1-x}As:Zn$ deposition	840	700	10 (50)	0↗2 (500)	12 (100)	2	350
	$Al_xGa_{1-x}As:Zn$ deposition	660	700	10 (50)	2↗4 (500)	15 (100)	2	350
	$Al_xGa_{1-x}As:Zn$ deposition	360	700	10 (50)	4↗6 (500)	15 (100)	2	350
	$Al_xGa_{1-x}As:Zn$ deposition	240	700	10 (50)	6↗8 (500)	15 (100)	2	350
Sample B	$Al_xGa_{1-x}As:Zn$ deposition	960	700	10 (50)	0↗1 (500)	15 (100)	2	350
	$Al_xGa_{1-x}As:Zn$ deposition	690	700	10 (50)	1↗2 (500)	15↗20 (100)	2	350
	$Al_xGa_{1-x}As:Zn$ deposition	390	700	10 (50)	2↗4 (500)	20 (100)	2	350
	$Al_xGa_{1-x}As:Zn$ deposition	270	700	10 (50)	4↗6 (500)	20 (100)	2	350
	$Al_xGa_{1-x}As:Zn$ deposition	270	700	10 (50)	6↗8 (500)	20 (100)	2	350
	Flow stabilization	120	700	10 (50)	50 (10)	70 (100)	2	350
	GaAs:Zn deposition	140	700	10 (50)	50 (10)	70 (100)	2	350
	Cooling		↘20					

was deposited. Then compositionally graded $Al_xGa_{1-x}As:Zn$ layer was grown according to the new multistage procedure. Two approaches with 4 (sample A) and 5 (sample B) stages processes were carried out. Conditions of each period have been selected in the way to confirm the best fit to expected profile of aluminum content and constant doping level. A detailed description of MOVPE process is presented in Tab. 2 and Fig. 6.

The properties of sample A and sample B were investigated by PVS, ECV and SIMS methods to check the modeling accuracy and for comparison of the new multistage procedure with previously described single stage one. Details of the results obtained are presented in Fig. 7. Profiles of Al content (Fig. 7**a**) measured for sample A and sample B by PVS method have almost a linear dependence of depth. SIMS measurement also confirms better realization of expected theoretical Al content profile of deposited structure. The total thickness of FGM layer varies from 0.4 μm to 0.6 μm depending on the measurement method, which is shifted by about ±20% from expected one (Fig. 2). The estimated gradient of Al content was about 0.0007–0.0009 nm^{-1}. Doping levels of *p*-region of sample A and B differ because of the different substrates which were applied for epitaxial growth – conducted and semi-insulated in the case of

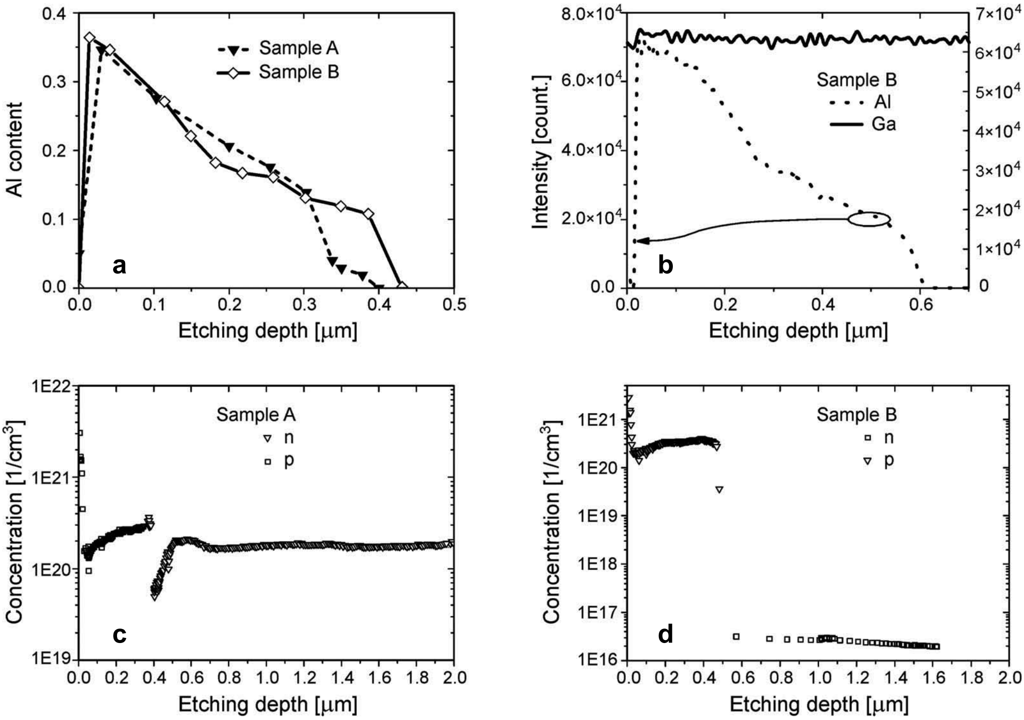

Fig. 7. PVS (**a**), SIMS (**b**) and ECV (**c**, **d**) profiles of composition and doping of compositionally graded structure of $Al_xGa_{1-x}As/GaAs$ photodetector deposited according to the multistage procedure developed.

sample A and B, respectively. Also, the obtained doping levels of sample A and B were higher than theoretical ones because of technological requirements concerning good ohmic contact to semiconductor structure. Doping uniformity in *p*-region was quite good and varied from 1×10^{20} cm^{-3} to 5×10^{20} cm^{-3} for both samples.

3. Conclusions and future work

A new method of MOVPE process design, based on multistage growth procedure was applied to obtain required graded Al content profiles and constant doping levels, simultaneously. Our experiments proved that advanced process design procedures, including dynamic calibration and additional processes runs, allowed us to fabricate the epitaxial structures of FGM photodetector structures with appropriate parameters.

Future work will be focused on automating the design of MOVPE growth process of compositionally graded $Al_xGa_{1-x}As/GaAs$ structures for optoelectronic applications. More sophisticated methods, such as computer-aided design and neural networks, will be applied for accurate epitaxial process design and simulation.

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