Study of the Gallium Arsenide Layers Growing Process on the Own Oxide Surface by HVPE Method

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***Abstract* - At the moment the global capacity of the solar energy installed in the electrical (grid) network exceed 100 GW while in 2000 it was 1,5 GW. But the efficiency of photovoltaic module remains at the silicon electro physical properties level, which makes the direct method of sun energy conversion competitive compared to traditional methods which are dangerous for the environment. The utilization of A_3B_5 semiconductor compounds manufacture increases over 40% of module photovoltaic efficiency, but it is not commercially competitive for terrestrial applications. Automation hydride vapor phase eptaxy (HVPE) technology of growing gallium arsenide (GaAs) epitaxial layers on own oxide substrate in Ga-$AsCl_3$ –H_2 gas system permits the exclusion of massive GaAs substrate and consequently the decrease of production costs of efficient photovoltaic cells. The investigated results of this technology are presented in the report and they are confirmed by experiments with obtained structures. It was used the AFM, RAMAN spectroscopy of investigation, electrical and optical measurements.**

Keywords*—*gallium arsenide layer; hydride vapor phase epitaxy; oxide substrate; Raman spectroscopy.

I. INTRODUCTION

The data concerning electrical solar energetics, brought up-to-date in August 1, 2014, show the global solar capacity of 100 GW. We remind that to assimilate this result the industrial monitoring began from 1,5 GW in the 2000 year. According to the UK center of climate and solutions data the sun is the most dynamic source of regenerative electricity. We mention that at the moment there are the following solar technologies, which demonstrated their work in industrial applications with different competitiveness. They are:

Solar photovoltaic *(Photovoltaic, PV)* –photo-sensible semiconductors layers create a flux of electrons when the sunray lights them up. PV doesn't require direct solar radiation it can work in low illumination conditions.

Solar heating *(Solar thermal)* – a pipe system with water absorbs solar heat for stocking it and utilizing in different applications.

Solar thermal/electric power plants *(Concentrating solar power)* – a system of mirrors or lenses concentrates the solar energy into a heat flux which produces steam that is used to power a generator of electricity.

A fourth method is the photovoltaic/thermal *(PVT)* – a combination between PV and solar thermal which exploits simultaneously the most performing properties of both methods including utilizing concentrated radiation with photovoltaic.

The trend of technological researches and innovations in photovoltaic is reaching the purpose of maximal efficiency of conversion by passing from tandem construction of photovoltaic cells (three junctions) with 42,6% of efficiency [1], also from technological problems of the p-n junction adjusting, to the construction into semiconductor energy of an intermediary band for solar bands (IBSC) using new modern nano-technology based on methods and conventional equipments.

In industry the photovoltaic engineering is the propeller for a new record of PV efficiency up to 43,6% with a level energy concentration of 319 (319 suns) announced in 2013 by Soitec, Inc. [2]. The new cell has demonstrated more than 43 percent of energy-generating efficiency over a concentration range between 250 and 500. The innovative four-junction cell uses two new, highly sophisticated dual-junction sub cells grown on different III-V compound materials, which allows optimal band-gap combinations tailored to capture a broader range of the solar spectrum. This maximizes energy-generating efficiency [2]. The well-known advanced semiconductor-bonding and layer-transfer technologies are made possible to stack non-lattice-matched materials while also raising the possibility of re-using expensive materials.

The power conversion efficiency of solar modules through improved materials, device designs and strategies for light management can increase by mechanical stacking of independent multi-junction cells [3]. These authors are demonstrated quadruple-junction, four-terminal solar cells with measured efficiencies of 43.9% at concentrations exceeding 1,000 suns, and modules with efficiencies of 36.5%. It is expecting power efficiency of solar sell more than 50%.

Following the objective of efficiency increase and price diminution of PV devices the industry of terrestrial applications is orientating to use A^3B^5 compounds materials [4], although *rol-to-rol* technology *(Nanosolar Inc.)* shows exceptions at the productivity and technological losses up to 3% for pure semiconductor materials as Cu(InGa)Se2 [5,6].

Authors of this report have as goal the terrestrial applications of solar cells and as objective growing gallium arsenide (GaAs) epitaxial layers on surface of own oxide by hydride vapor phase epitaxy (HVPE) in Ga – $AsCl_3$ – H_2 gas system. Oxide layer was modeled on the [100] surface of a GaAs plate used in industry to produce different planar semiconductor structures as power devices. It will be modeled on the metallic surfaces in the future.

II. Experimental

A. *Oxide deposition on GaAs surface.*

Modeling of gallium oxide was carried out on GaAs industrial plate of [100] oriented, AGCZ-30b of type doped with zinc for $p^+ = 2x10^{18}$ cm^{-3} of concentration. Chemical method of oxide layer deposition selected by small prices is characterized by non-homogeneous local reaction speeds loss on the semiconductor surface in function of the defect nature on the plate surface. To exclude the surface metallurgical defects was implemented by growing a GaAs planar layer with $p^+ = 4x10^{18}$ cm^{-3} of concentration and 7μ of thickness by HVPE technology with reaction transport.

Etched solution was prepared by mixing nitric acid and concentrated hydrochloric acid (HNO_3: HCl) and stocking it for four hours at chamber temperature. GaAs plate with homogenized by epitaxial surfaces was installed on vacuum valve support. Selected surface of plate was contacted with surface of acid solution for 10-90 s. at the temperature of chamber, than it was washed in the de-ionized water and dried in acetone. After the deposition the plate was introduced in the furnace at 320 °C of temperature for 5 min. Temperature treatment in gas mix of nitrogen and oxygen was produced in the quartz reactor at 550 °C of the temperature. Thickness of the oxide layer was 200-300 nm.

B. *Formation of p-n junction on oxide surface.*

Layers of GaAs on oxide surface were grown in ICE-3/4R reaction plant by known conventional conditions (program) of planar epitaxial structures manufacturing. Before being introduced in reactor the oxidized plate according to p. 2.1 was degreased by boiling in toluene, etched in solution $2NH_4OH + 1H_2O_2 + 7H_2O$ than washed in de-ionized water and dried in acetone.

The first epitaxial layer on oxide has a thickness of 9-11 μ and the concentration of charge carrier $p^o = 4x10^{17}cm^{-3}$. The second epitaxial layer of GaAs doped with tellurium at the charge carrier of $n^+ = 10^{19}$ cm^{-3} with thickness of 3 μ was grown in the continuation of the same technological process [7] in the reactor (720 °C in the deposition area). Thus it was obtained a p-n junction on oxide substrate.

C. *Research methods.*

The methodology for the study of this technological process was selected to identify more problems relied on the engineering of GaAs layers deposition on oxide substrate in the reactor of technological installation by the known method [7] of epitaxy with the reaction transport.

Morphology of oxide layer obtained on advanced metallurgical microscope MM-500T (US) is shown in fig. 1. Micro-textured image of the structure demonstrates the complex character of the technological process and requires experimental studies of the layers at different stages of the technological process.

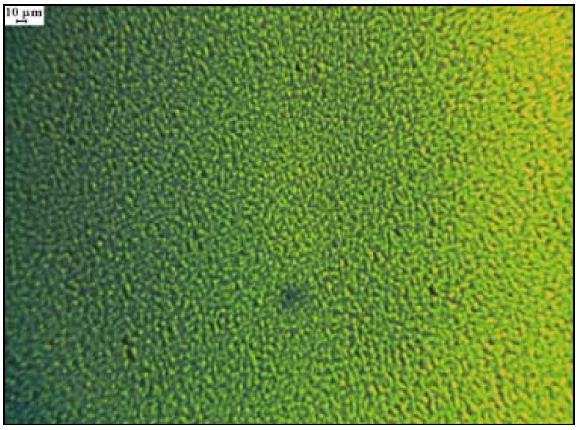

Fig. 1. Oxide layer image on GaAs plate on MM-500T micriscope.

We observe in fig. 2. (Left position) that the light

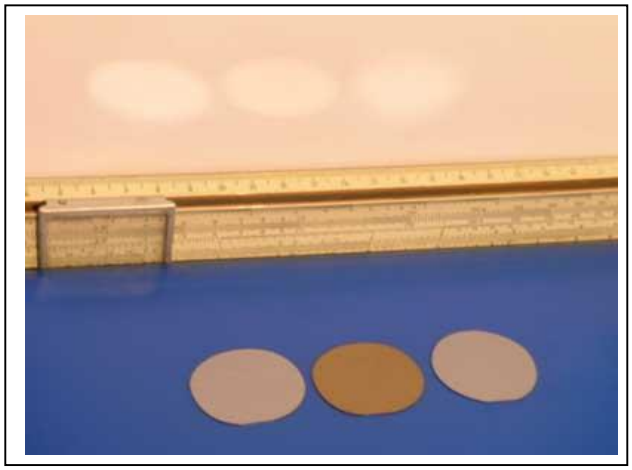

Fig. 2. Image of reflected light from GaAs plate surface at three stages of technological process: before oxidation epitaxial, oxidation and after oxidation epitaxial.

Reflection on the screen from the surface of GaAs substrate with epitaxial layer, prepared for the oxidation process, has a clear image (in the left). Central position of the image is less clear and represents the oxide layer obtained as a result of chemical reaction in the

technological process described above. On the right side fig. 2 is positioned the image of epitaxial layer grown on oxide substrate, which lost the outline of the GaAs initial plate.

Spectral method of combined diffusion (Raman) was used to identify the layers obtained on technological route. It was used the MonoVista Confocal Raman Spectrometer with optional laser 542 nm CW (continuous wave), diffraction grating 2400 g/mm, resolution 0.5 cm^{-1}, spot size 1-2 μm (Germany). The essential feature of this apparatus is the excessive intensity of the exciting flux reaching a few hundred kW/cm^2, which can cause changes in the investigated layers particularly in the oxide layer. This requires an adjustment device to the study samples.

The result of the spectrometer adjustment to oxide layer deposited on GaAs plate in the described conditions is shown in fig. 3. By Raman spectra recording of oxide layer at different intensity of the exciting flux. For analyzing in identical conditions there were recorded the Raman spectra of p-GaAs as initial substrate and n-GaAs epitaxial layer grown on gallium oxide surface.

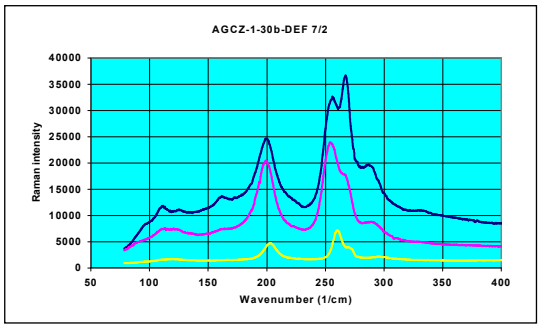

Fig. 3. Raman spectrum of oxide layer deposited on p-GaAs substrate at three different intensities of luminous exciting fluxes.

Images from fig. 3 demonstrate that the intensity of exciting flux changes essentially the Raman spectrum composition of the oxide layer. There are appearing GaAs characteristic bands as 114cm^{-1}, 296cm^{-1}. Band of 270cm^{-1} grows up with the exciting intensity exceeding the band with maximum Raman intensity of 261cm^{-1}. Also there is observed the change of place 204 cm^{-1} of band to 200 cm^{-1}, probably determined by 192 cm^{-1} of band characterized to GaAs material. Finally it was selected an intensity of minimum excitement when there are observed the studying layers characteristic bands.

III. RESULTS AND DISCUSSION

A. Raman spectrum analysis

Raman spectroscopy of GaAs substrates used in the experiments demonstrates that spectrums have the same components indifferently of conductibility type of semiconductor. As initial substrate the p-GaAs has the spectrum shown in fig. 4. Here we distinguish three main characteristic bands 114, 193, 296 cm^{-1} and two bands with the small intensity 122 and 273 cm^{-1}.

Raman spectroscopy was used by Yanyan Zhao [8,9] to characterize both gallium oxyhydroxide (α-GaO(OH)) and gallium oxide (β-Ga_2O_3) nanorods synthesised with and without the surfactants using a soft chemical methodology at low temperatures.

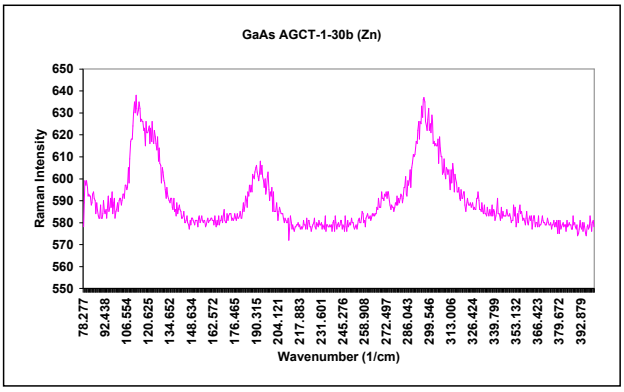

Fig. 4. Raman spectrum of p-GaAs as substrate for Oxide deposition.

We will attempt to identify the oxide layer in our experience also carried out in low temperature conditions. Look at the Raman spectrum of oxide layer in our experiments in fig. 5. The characteristic bands are 203 cm^{-1}, 261 cm^{-1} and 270 cm^{-1}.

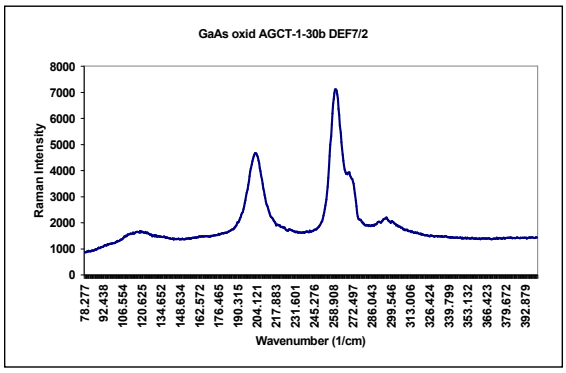

Fig. 5 Raman spectrum of own oxide on p-GaAs substrate.

This bands of Raman spectroscopy are assigned to vibrational modes involving Ga-OH deformation modes [8]. So we have the Raman spectra bands characteristic of the GaO(OH), wich can be converting upon calcination to β-gallium oxide at the temperature more than 900 °C. Modification of β-gallium oxide is chemically stable and has 1725 °C of melting temperature. The α-gallium oxyhydroxide is not stable and studying layer of oxide on GaAs being introduced in reactor aria with 720-740 °C of temperature in hydrogen flux can be reduced up to gallium metallic. Therefore the morphology of this oxide layer can influences the growing process of GaAs epitaxial layer, thus it contributes to other crystalline structure formation as relief structures.

The epitaxial GaAs grown on oxide substrate has the same bands of Raman spectrum as the initial plate in our experiments fig. 6. The bands of epi-GaAs are 114

cm^{-1}, 193 cm^{-1}, 296 cm^{-1}, which demonstrates the possibility of achievement of the epitaxial technology with reaction transport in growing of GaAs photovoltaic structure on other substrates than one for instance metallic substrates.

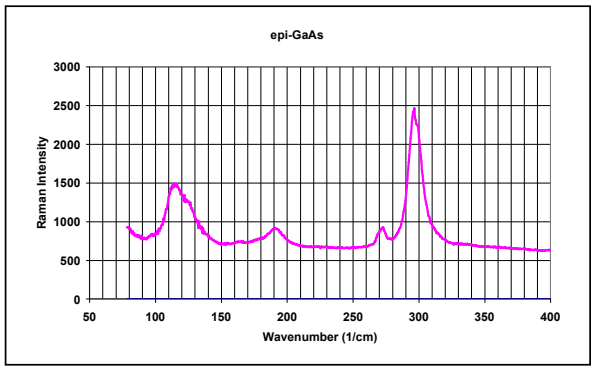

Fig. 6. Raman spectrum of GaAs epitaxial layer grown on own oxide.

Raman testing result of the initial, intermediary and final layers in technological process of GaAs photovoltaic structures growth is presented in table 1.

TABLE I. RAMAN SPECTRA OF GALLIUM ARSENIDE SUBSTRATE (A), GALLIUM OXIDE (B) AND EPITAXIAL GROWN ON OXIDE LAYERS (C)

Test	Raman spectra bands, cm^{-1}								
A	114		122	193	-	-		273	296
B	-	120	-	-	203	261	270	-	296
C	116	-	-	193	-	-	-	273	296

Raman spectroscopy was used to investigate the forming process and the structure of layers utilized at photovoltaic cells production with overhung p-n junction. Remained out of the present investigation are the references about bands of less intensity 122 cm^{-1} and 173 cm^{-1}in GaAs Raman spectrum and respectively the band of 296 cm^{-1} in the oxide layer spectrum. Most likely the thickness of oxide layer smaller than one micron and GaAs plate oxidation at chamber temperature are the reasons of the appearance in the spectra of these bands of small intensity.

IV. CONCLUSION

The technological experiments investigated in this work demonstrated that the HVPE method of GaAs epitaxy with reaction transport in Ga-$AsCl_3$-H_2 gas system is valuable and can be utilized for epitaxial structures grown on supports of other materials than semiconductor A^3B^5 as metals or materials with multiple micro defects on surface, which can be used in technological process as crystallization centers. Development of this technology in the direction of diminishing the texture dimensions on epitaxial layer up to quantum effect can reduce the production expenses and essentially increase the conversion efficiency of photovoltaic cells.

REFERENCES

[1] Qu Xiaosheng, Zhang Sisi, Bao Hongyin and Xiong Liling, „The effect of InAs quantum-dot size and interdot distance on GaInP/GaAs/GaInAs/Ge multi-jonction tandem solar cells," *Jurnal of semiconductors*, vol. 34, No. 6, 2013.

[2] Andre-Jacques Auberton-Herve. "*Four-Junction Solar Cell achieves peak efficiency of 43.6%."* May 30, 2013, http://news.thomasnet.com/fullstory/Four-Junction-Solar-Cell-achieves-peak-efficiency-of-43-6-20008879

[3] Xing Sheng and al. "Printing-based assembly of quadruple-junction four-terminal microscale solar cells and their use in high-efficiency modules," *Nature Materials 13, 2014, pp. 593–598.*

[4] B.D. Jozce, J.B. Mullin, „Obrayovanie Piramid v Epitaxialinih Plencah GaAs," V sbornike „*Arsenid Gallia"* per. s angl., pod red. A.A. Vizel, Sovetscoe Radio, M., 1972, pp. 36-40.

[5] Martin LaMonica „*Thin-Film Solar Upstart Nanosolar Slims Down*," February 19, 2013, http://www.technologyreview.com/view/511441/thin-film-solar-upstart-nanosolar-slims-down/

[6] *Van Ben Chu* et al., „Fabrication of solution processed 3D nanostructured $CuInGaS_2$ thin film solar cells," *Nanotechnology*, vol. **25**, 2014, doi:10.1088/0957-4484/25/12/125401.

[7] S. Baranov, B. Cinic, L. Gorceac „*Procedeu de fabricare a dispozitivului semiconductor cu joncţiune p-n în relief (variante),"* MD Patent Document nr.4261, MD-BOPI, 12/2013, pp. 21-23.

[8] Yanyan Zhao, Jing Yang, L. Ray, Frost, "Raman spectroscopy of the transition of α-gallium oxyhydroxide to β-gallium oxide nanorods" *Journal of Raman Spectroscopy*. Vol. 39, Issue 10, October 2008, pp. 1327–1331.

[9] Yanyan Zhao, L. Ray, Frost, "Raman spectroscopy and characterisation of α-gallium oxyhydroxide and β-gallium oxide nanorods," *Journal of Raman Spectroscopy*. Vol. 39, Issue 10, October 2008, pp. 1494–1501.