Solar cell technology on the base of III-V heterostructures

P Vitanov¹, M Milanova², E Goranova¹, Ch Dikov¹, Pl Ivanov¹ and V Bakardjieva¹

¹Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72, Tzarigradsko Chaussee Boulevard, 1784 Sofia, Bulgaria,
²Central Laboratory of Applied Physics, 59, St.Petersburg Boulevard, 4000 Plovdiv, Bulgaria

E-mail: vitanov@phys.bas.bg

Abstract. Low-cost single-junction GaAs solar cells on the base of p-AlGaAs/p-GaAs/n-GaAs heterostructures grown by low-temperature liquid-phase epitaxy have been fabricated. For analyzing the factors contributing to solar cell efficiency the program products PC1D have been used. The optimal doping concentrations and thicknesses of the layers which correspond to the maximum values of the solar cell output parameters have been determined. The multilayer solar cell structure has been optimized on the base of this simulation. Low cost technological processes and masks, necessary for fabrication of the cells on the base of the grown heterostructures, have been developed, too. The front and back metallization of the cell is Ni/Al system deposited by magnetron sputtering. A double layer Al₂O₃/ZrO₂ antireflection coating is deposited on the front side of a solar cell structure by the spin coating technique. The conversion efficiencies of 19 % at one sun AM1.5 conditions have been measured.

1. Introduction

As shown previously [1-3] high-efficiency solar cells with enhanced spectral response can be developed on AlₓGa₁₋ₓAs/GaAs heterostructures. Conversion efficiencies up to 25% at (AM1.5) one sun illumination and 27-28 % at concentrated light were obtained, as well. Recently, interest in the GaAs single junction is raised again. The new concepts is the use of films of GaAs or AlGaAs grown in thick, multilayer epitaxial assemblies, then separated from each other and distributed on foreign substrates by printing [4].

Melt-grown epitaxial films, prepared by low temperature Liquid Phase Epitaxy (LPE), are successfully used [5, 6] to fabricate high-quality multilayer AlGaAs/GaAs heterostructures containing layers as thin as 2-20 nm combined with several microns thick ones and having a smooth surface and flat interfaces.

In this paper, we investigate thin film multilayer heterostructures for solar cell application, grown by low temperature LPE. The aim of the investigations is to optimize the layer thickness, doping and composition, in order to ensure high efficiency solar cell preparation.

2. Heterostructure preparation

2.1. Epitaxy
The AlGaAs/GaAs multilayer heterostructures are grown in a horizontal LPE reactor using multiple bin “piston” boat on n-type (100) oriented 15×20 mm GaAs substrate. In order to reduce the growth rate for preparing thin layers we use Ga-melt only 500 µm thick and the growth temperature is lowered down to 480°C where the As-fraction in the melt becomes too low. In the used piston boat the substrate surface after the first wetting stays always covered by the melt. The latter ensures wetting of Al-containing melts at low growth temperature in the range 500-600°C which is a very difficult problem during the AlGaAs heterostructures preparing. The source materials used in the melt are pure Ga (6N) and Al and undoped boat-grown polycrystalline GaAs. The dopants are: Te for n-type GaAs and Ge or Mg for p-type GaAs and AlGaAs layers. The growth is carried out in a purified H₂ gas flow after pre-heating of the charged boat at 800°C for 1h in order to decrease the contaminations of the residual impurities in the melt. The initial epitaxy temperature was 670°C and the p-n junction was formed at 520°C. The thin AlGaAs window layer was deposited at 480°C.

2.2. Samples structure
The investigated heterostructures for high efficiency solar cell application contain 5 epitaxial films melt-grown on n-GaAs substrate: a AlGaAs buffer layer, a n-type GaAs layer as a base, a p⁺ type GaAs emitter, an ultra-thin AlGaAs “window” layer, and a thin heavily doped p⁺-type GaAs contact layer. The latter forms a stable low-resistance contact to the p-side and protects the window layer during the production processes. As back surface field, the introduction of potential barrier at the back of the base improves the collection efficiency of the minority carriers generated in the photoactive region. This barrier is made by growing a n-type AlₓGa₁₋ₓAs buffer layer on a GaAs substrate. The surface recombination on the front side of the solar cell can be minimized by depositing an ultra-thin film (window layer) of wide band gap material and transparent to short-wavelength light. In our case that is AlₓGa₁₋ₓAs with 80-85 % AlAs content.

For analyzing the factors, contributing to solar cell efficiency the solar cell simulator PC1D was used [7]. The effect of layers' thickness on the window and emitter layers as well as the doping of the window, the base and the emitter layers on the device efficiency was assessed. The multilayer structure of the solar cell was optimized on the base on these results. The scheme of optimized structure grown in this work is shown in the figure 1.

| Layer | Thickness (µm) | Composition |
|-------|----------------|-------------|
| CAP   | 0.2 - 0.3      | p⁺-GaAs     |
| WINDOW| 0.02 - 0.05    | p⁺-AlₓGa₁₋ₓAs |
| EMITTER | 1 - 1.5      | p⁺-GaAs     |
| BASE  | 30 - 40        | n⁻-GaAs     |
| BSF LAYER | 20 - 30   | n⁻-AlₓGa₁₋ₓAs |
| SUBSTRATE | 400          | n⁻-GaAs     |

**Figure 1.** Schematic diagram of the optimized multilayer AlGaAs/GaAs structure for solar cell application.

**Figure 2.** Cross-sectional view of the heterostructure: Substrate; 1 - BSF layer, 4µm; 2-Base, 3.1µm; 3 - Emitter, 1.5µm; 4 - Window layer; 5 - Capping layer, 0.2 µm

3. Heterostructure characterization
The layer thickness is measured on (110) cleaved cross-sections using SEM and optical microscopes. Figure 2 shows an optical photomicrograph of the heterostructure. The latter shows layers in a compositional contrast since their colours are different due to the different band gap energy. The first and the fourth wide-gap layers seem darker. They are nearly equal in colour, actually violet in the used
colour gamma. The nanoscale window layer 4 is seen just like an interface between the area of the layers 3 and 4. The measured thicknesses of the layers are near the technologically predicted ones: 4 µm for the BSF layer 1, 3.1 µm for the base 2, 1.5 µm for the emitter 3 and 0.2 µm for the capping layer 5. The window layer 4 is estimated to be less than 0.1 µm in the limits of the optical measurements. Figure 2 shows also that the interfaces are flat and of a good quality without macroscopic defects.

The molar fraction of AlAs in the ternary AlGaAs solid solution measured on the same cross-section by EDAX technique in BSF regions x = 0.23.

The thicknesses and composition of the “window” layer are estimated by a combination of Raman scattering with anodic oxidation method [8]. The principle of this method is a precise step of the anodization structures and subsequent detection of the Raman spectra. Analysis of the Raman intensity and Raman shift on the thickness of the anodization material make it possible to estimate the thickness and composition values of the layer. Anodic oxidation of the heterostructures was performed in tartaric acid-glycol-water electrolytes. The consumption material rate was found to be 1nm/V. The Raman measurements were performed at room temperature in the backscattering configuration. The sample was excited by the 514.5 nm line of an Ar+ ion laser. In order to determine the thickness and composition of the window layer the solar cell structures without heavily doped p+GaAs layer on the surface were grown.

Figure 3 presents the Raman spectra of the one as grown structure (curve 1) and after anodic oxidation at anodic voltage 30 and 40 V (curves 2 and 3, respectively). Since in back scattering geometry along [100] the transverse optical phonon (TO) frequency is forbidden for the zinc-blend compounds only the longitudinal optical (LO) phonon peak shifts appeared.

Raman spectra of AlGaAs give two mode optical phonon frequencies of GaAs like LO1 phonon and AlAs like LO2 phonon. The peak shift at 262 cm⁻¹ of LO1 phonon and 396 cm⁻¹ of LO2 phonon were measured of the as grown structure. Using the dependence of the frequencies of the LO phonons in mixed AlₓGa₁₋ₓAs crystals as a function of the composition x, established by the authors of ref. [8, 9] we determined the AlAs content in the window layer to be about 80%. The LO phonon peak shift seen at 292 cm⁻¹ is coming from the GaAs emitter. Analysis of Raman spectra of the structure after precisely etching of the window layer at each stage of oxidation allowed us to evaluate the window thickness of about 40 nm. After step oxidation of the structure at 10, 20 and 30 V the intensity of the
optical phonons of the window layer drops in accordance with the decrease of the window thickness. As seen in the figure after oxidation of 30 nm of the structure (curve 2) a weak LO1 and LO2 peak shift from very thin graded composition AlGaAs window were measured. Further oxidation of the structures at 40 V (curve 3) leads to the fully etched of the window layer and the Raman spectra gives only LO phonon peak shift of the GaAs emitter layer with high intensity.

The separate control layers of heterostructures grown on semi insulating GaAs substrates are characterized by Hall-effect measurements. Carrier concentration n and Hall mobility μ in the range of 80 - 300 K are measured. The temperature rates of n and μ for the n-type base layer of the structures are shown in figure 4. Reasonable values and behaviour are obtained which correspond to good quality epitaxial layers.

These results have been applied at AlGaAs/GaAs solar cell fabrication.

4. Solar cell processing and results

4.1 Solar cell design

A set of 4 masks for a chip with a multiplication step of 2.75 mm is developed. Solar cells (2.5 x 2.5 mm² in size with a circle illumination area of 3.14 mm²) are prepared. With mask 1 the contact p⁺GaAs thin surface layer is etched off selectively until the window is open in the regions outside the contact grid. The front metal grid is defined by lift off photolithography with mask 2. The width of the metal lines is 8 μm, while the space (illuminated window) between the lines is 92 μm. The front and back metallization of the cell is Ni/Al system deposited by magnetron sputtering. A typical specific resistance of 5.10⁻⁵ Ohm.cm was achieved for n-type contact and higher than 10⁻⁴ Ohm.cm for p-type contact.

Figure 5. A photograph of a multilayer AlGaAs/GaAs based solar cell.

Figure 6. A detail view of the metal grid front side.

The cell has a double antireflection coating (ARC), Al₂O₃ (45 nm) on a top of ZrO₂ (49 nm) with the refractive index equal to 1.48 and 1.9 respectively. A double layer ARC is deposited on the front side of a AlGaAs/GaAs solar cell by the spin coating technique - a cheap, non expensive method with fairly reproducible results. The optimal thickness of the two layers was determined by minimization of the average weighted reflection [10]. A theoretical value of 2.17% is reached for top layer (Al₂O₃) thickness of 45 nm and bottom layer (ZrO₂) thickness of 49 nm. The double-layer ARC on the contact pads is removed with mask 3 and the coating remains only on the solar cell active area - the central
circle with diameter 2 mm. Finally, a mesa etching is applied using mask 4 in order to isolate each solar cell on the wafer.

A solar cell structure without $p^+GaAs$ contact layer on the surface and with two region emitter: the main region with optimal parameters determinated from the simulation process and an additional heavily doped emitter layer grown on the top of the main region in order to ensure good ohmic contact [2] is realized, too. This technological version is preferred because thus the total number of masks is reduced to three.

4.2 Results
An automatic measuring system under standard test conditions AM1.5 is used to assess the solar cell basic parameters: short-circuit current $J_{sc}$, open-circuit $V_{oc}$, fill factor FF and conversion efficiency $\eta$.

Figures 7a and 7b show typical I-V curves of the two types of cells measured under standard test conditions.

![Figure 7a](image1.png)  ![Figure 7b](image2.png)

**Figure 7a.** Experimental I-V curve of typical AlGaAs/GaAs based solar cell with cap layer.  **Figure 7b.** Experimental I-V curve of typical AlGaAs/GaAs based solar cell without cap layer.

The substrates used for epitaxial growth are of dimensions $15 \times 20$ mm and the 22 chips of the solar cells are formed on them. Typical values of conversion efficiency $\eta$ of 18.7 % ($J_{sc}=29.87$ mA, $V_{oc}=0.92$V, FF=0.68) were obtained for the most chips for sample E86 which is without cap layer. The best measured values are 19.5% which is a very good result for one-junction solar cells. The deviation of 1.5 % for all 22 cells is due to the possible defects of the technological realization which is made at laboratory conditions and not at “clean room” conditions. Comparable conversion efficiencies exhibit the samples with $p^+$ GaAs cap on the surface.

5. Conclusions
Multilayer heterostructures have been grown by low temperature Liquid Phase Epitaxy on a heavily doped $n^+$GaAs substrate. The solar cell simulator PC1D 4.5 is used to optimize the epitaxial layer thickness and doping concentrations. Electron concentration and Hall mobility are investigated on test structures grown on semiinsulating substrates. Results show that epitaxial layers of very good crystalline properties are prepared by LPE. The technological processes and the masks, necessary for the fabrication of devices based on AlGaAs/GaAs heterostructures have been developed and solar cells with the best conversion efficiency of 19.5% under AM1.5 one sun conditions fabricated.

Acknowledgements
This work has been financed by the Ministry of Education and Science of Bulgaria under the contract D-01-369/2006.
References

[1] Tobin S P, Vernon S M, Bajgaret C, Wojtczuk S, Melloch M R, Keshavarzi A, Stellwag T B, 
Venkatensan S, Lundstrom M and Emery K A 1990 *IEEE Trans. Electr. Dev.* 37 469

[2] Algora C, Ortiz E, Rey-Stolle I, Diaz V, Pena R, Andreev V M, Khvostikov V P and 
Rumyantsev V D, 2001 *IEEE Trans. Elec. Dev.* 48 840

[3] Andreev V M, Khvostikov V P, Larionov R, Rumyantsev V D, Paleeva E V and M. Shvartz M 
Z 1999 *Fiz. Tekh. Poluprovodn.* 33 1070

[4] Yoon J, Jo S, Chun I S, Jung I, Kim H, Meitl M, Menard E, Li X, Coleman J J, Paik U, Rogers J 
A, 2010 *Nature* 465 329

[5] Andreev V M, Kazantsev A B, Khvostikov V P, Paleeva E V, Rumyantsev V D, Sorokina S V, 
1996 *Mat. Chem. and Physics* 45 130

[6] Milanova M and Khvostikov V 2000 *J. Cryst. Growth* 219 193

[7] Ivanov P, Vitanov P, Goranova E, Milanova M, Kakanakov R and Alexieva T 2009 *J. Optoel. 
Adv. Mater.* 1 238

[8] Andreev V M, Mintairov A M, Nahimovich V D, Rumyantsev V D, Khvostikov V P, Yakimov 
A Yu 1989 *Proc. Sov. Conf. Solid-State Electronics* (*Leningrad, USSR ,1989 vol B*) pp 
102-103

[9] Andreev V M, Larionov V R, Mintairov A M, Prutskih T A, Rumyantsev V D, Smekalin K E 
and Khvostikov V P 1990 *Tech. Phys. Let. (Russ.)* 16 7

[10] Alexieva Z I, Nenova Z S, Bakardjieva V S, Milanova M M and Dikov Hr 2010 *J. Phys.: 
Conference Series* 223 01204