LOW-BANDGAP PV AND THERMOPHOTOVOLTAIC CELLS

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ABSTRACT

The performance of GaSb cells was improved by optimization of diffused emitter, which allowed increasing efficiencies up to 11% under AM0 spectrum and 19% under the part of AM0 spectrum with $\lambda > 900$ nm at photocurrent of 2-7 A/cm^2.

By means of LPE growth and Zn diffusion, TPV cells based on (*p-n*)-InAsSbP/*n*-InAs and (*p-n*)-InAs structures sensitive in the range of (2.5-3.4) μm were fabricated.

Zinc-diffused (*p-n*)-Ge based PV cells were fabricated with short circuit current density of 31.6 mA/cm^2 at 8% shadowing and of 33.2 mA/cm^2 obtained from the spectral curve of the internal quantum yield at active area under sunlight with $\lambda > 900$ nm AM0 spectrum. Ge cells with GaAs windows were developed by the combination of LPE or MOCVD growth of GaAs and Zn–diffusion. Efficiency higher than 13% was obtained in *p*-GaAs/(*p-n*)-Ge cells with under cut off $\lambda > 900$ nm AM0 spectrum at photocurrent densities of 3-25 A/cm^2.

1. INTRODUCTION

Theoretical simulation has shown that optimal bandgap energy lies in the range of 0.75 – 0.4 eV in TPV cells operating with a blackbody (graybody) emitter at temperatures of 1200-1500 ^{o}C. GaSb and Ge as the “bulk” materials are more fitting for energy conversion from IR emitter heated up to such temperatures. Low-bandgap semiconductors are also very promising as the bottom cells in multi-junction solar cells. GaSb was the first semiconductor successfully employed for preparation of TPV cells and of mechanically-stacked tandems. Recently intensive investigations of Ge-based cells were carried out as well, because Ge had become the basic material (as substrate and bottom cell) for manufacturing high efficiency multijunction solar cells.

Efficiency of TPV cells when used with a lower temperature blackbody heat source (1000-1200 ^{0}C) could be improved by extending the cut-off wavelength photosensitivity behind 2.0 μm [1-5]. With this point of view the GaSb/InGaAsSb and InAs based structures represent an important class of semiconductor materials, which are useful for the fabrication of such devices.

2. GaSb BASED CELLS

GaSb TPV cells with high quantum yield have been fabricated using a simple Zn-diffusion method without AlGaSb window layer. There is an additional opportunity to increase the photocurrent by reducing the *p-n*-junction thickness after Zn-diffusion. Precise etching [6] of structure after diffusion for 70-80 nm by anodic oxidation allows increasing the photocurrent due to the change both of the junction thickness and of a profile of impurity concentration. Fig.1 represents the efficiencies of GaSb based TPV cells with nano-etching emitters versus photocurrent density for different spectral ranges of AMO spectrum.

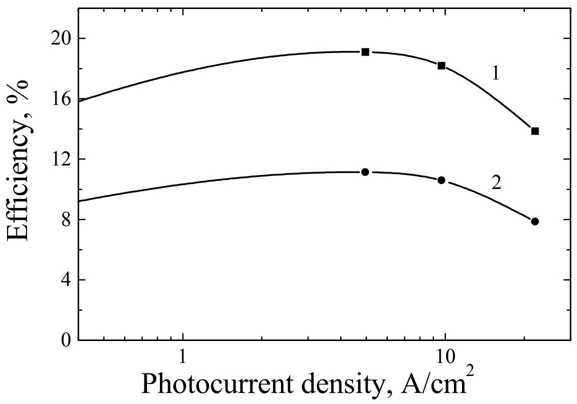

Fig. 1. Efficiencies of the GaSb TPV cell as a function of photocurrent density under AM0 spectrum: 1- efficiency in the wavelength range of 900-1820 nm, 2- efficiency in the wavelength range of 500-1820 nm.

3. InAs BASED TPV CELLS

The InAs-based TPV cells were fabricated by using wafers prepared from ingots grown by the Czochralski technique, Te-doped. The InAs “bulk” wafers were subjected to zinc diffusion procedure to form a *p-n* junction in photoactive area of the cells from a pure zinc source.

The *p*-InAs/*n*-InAs TPV cells demonstrate rather high external quantum yield of 60-70% up to 3.5 μm at room temperature. Higher photosensitivity can be obtained by growth of wide-bandgap lattice-matched window InAsSbP layer.

Narrow gap epitaxial InAsSbP (0.45-0.48eV) cells were fabricated from (*p-n*)-InAsSbP/*n*-InAs heterostructures grown on (100) *n*-InAs substrates. Growth of *n*-InAsSbP quaternary layers lattice matched to InAs has been carried out by LPE from the Sb-rich melt. The lattice-mismatch ratio $\Delta a / a$=0.15% was estimated from a X-ray diffraction pattern. The epitaxy was performed at 570^{0}C during 10 min (step-cooling technique) under 10-11^{0}C super-saturation conditions to avoid a composition gradient in the epitaxial layer.

The low-temperature (340-350 ^{o}C) pseudo-closed box Zn diffusion process was applied to form a *p-n* junction in the quaternary InAsSbP alloy. Fig.2 represents the spectral response of (*p-n*)-InAsSbP/*n*-InAs TPV cells. Reduction of photosensitivity in the long wavelength region is explained by not sufficient diffusion length for photogenerated holes in the epitaxial *n*-InAsSbP base layer.

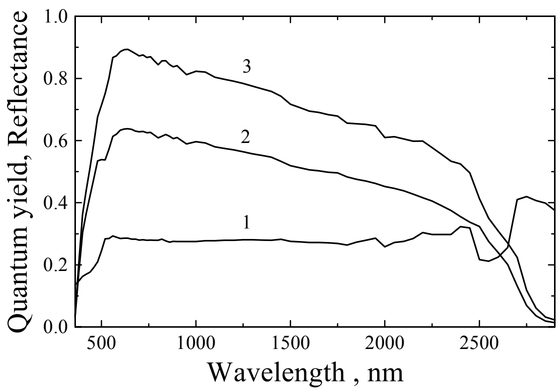

Fig. 2. Reflectance (1) and spectral responses (curve 2 - external and curve 3 - internal quantum yields) of the cell based on (*p-n*)-InAsSbP/*n*-InAs heterostructure.

4. Ge BASED CELLS

4.1 Zn-diffused (*p* – *n*)Ge cells

The pseudo-closed box Zn diffusion from vapor phase procedure was applied to form a *p-n* junction in *n*-Ge "bulk" wafers. Fabricated cells had an optimized MgF_2/ZnS ARC. The external quantum yield as high as 0.9 in the IR part of spectrum were measured in these Ge cells. Short circuit current density of 31.6 mA/ were obtained for cells cm^2 with 8% shadowing, illuminated by sunlight with the cut-off at $\lambda < 900$ nm AMO spectrum. $I_{sc} = 52.9$ mA/cm^2 was obtained for the same shadowing under AM0 spectrum cut off at $\lambda < 580$ nm. The calculated photocurrent density is 3.7 A/cm^2 under the radiation from blackbody emitter at temperature of 1473 K.

4.2 LPE grown and Zn-diffused *p*GaAs/*p*Ge-*n*Ge cells

The open circuit voltage of Ge cells is worse than that of previously developed GaSb based TPV cells. In order to improve this parameter the technology of LPE growth of a thin (0.1μm) GaAs window over Ge wafer has been developed.

TPV and PV cells on the *p*-GaAs/*p*-Ge/*n*-Ge heterostructure with a thin (0.1 μm) GaAs layer were fabricated by the low-temperature liquid-phase epitaxy and by an additional Zn-diffusion process into the *p*-GaAs-*n*-Ge heterostructure. The advantage of this technology compared to MOCVD, widely used now for fabrication of GaInP/GaAs/Ge triple-junction solar cells, is missing of undesirable diffusion of Ga and As atoms from vapour phase owing to much lower growth temperature.The growth was carried out at 380 ^{0}C from the supercooled liquid phase with a relatively fast cooling rate of 2 ^{0}C/sec in order to avoid dissolution of the Ge substrate. The short circuit current of 27.7 mA/cm^2 was measured under sunlight with the cut-off at $\lambda < 900$ nm AMO spectrum.

Fig.3 shows the *FF* and V_{oc} dependencies as a function of the generated in *p*-GaAs/*p*-Ge/*n*-Ge based cells photocurrent density in comparison with that for *p*-Ge/*n*-Ge cells. Fig.4 demostrates efficiency of Ge based PV cells with and without a GaAs window layer versus the photocurrent density. Efficiencies of higher than 13% under the cut-off ($\lambda < 900$ nm) solar AM0 spectrum have been achieved in PV cells with a GaAs window layer at the photocurrent densities of 3-25 A/cm^2 (curve 1). This efficiency seems to be the highest among those published for Ge-based cells measured in these conditions.

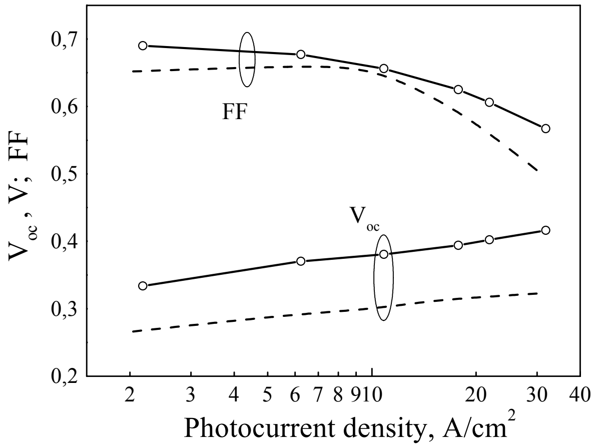

Fig. 3. Fill factor and open circuit voltage as a function of generated photocurrent density for Ge based cells: solid curves with open dots - with a GaAs wide gap window layer; dash curves - without a GaAs layer.

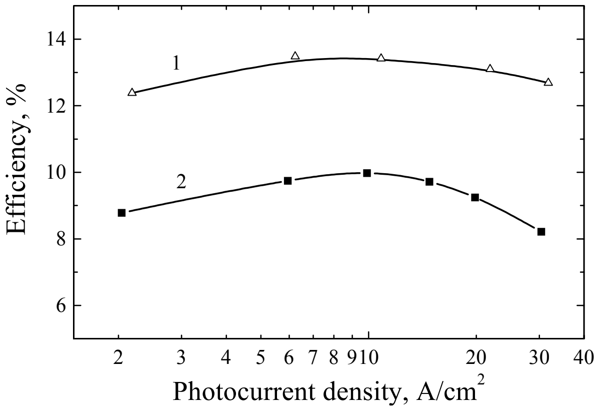

Fig. 4. Efficiency as a function of the photocurrent density for a Ge-based PV cell. Efficiency was calculated for illumination by sunlight with the cut-off at $\lambda < 900$ nm AM0 spectrum. Curve 1 - with a GaAs wide gap window layer; 2 - without a GaAs layer.

4.3 MOCVD grown and Zn-diffused *p*GaAs/*p*Ge-*n*Ge cells

An inevitable process of gallium arsenide growth on germanium by the MOCVD [7,8] technique is doping of Ge with As and Ga from the growing gallium arsenide layer. As it is seen from [8], the As diffusion depth in Ge is several μm, and the Ga diffusion depth in germanium is less than 1 μm. In lowering the growth temperature, the diffusion rates of arsenic and gallium decrease. The GaAs growth temperature in the given work was lowered from 680 down to 550°C, which ensures decreasing the diffusion coefficient of the growing layer by two orders of magnitude.

Growth of a wide-gap GaAs layer for the GaAs/Ge heterostructure was realized by the MOCVD technique on an installation of atmosphere pressure with a horizontal reactor. *n*-Ge doped with As was used for substrates. In the temperature range of 680-550˚C, the growth rate is determined by diffusion of the third group element (gallium) in the gas phase towards the growth surface and does not depend on temperature.

To obtain photocells on *n*-germanium substrates the following technological procedures for formation of photosensitive structures were investigated:

N1 - Planar Zn diffusion from the gas phase into the germanium substrate with the consequent growth of a layer of the wide-gap window (GaAs) with the additional Zn diffusion for doping this layer and with covering by an insulator to reduce current leakages.

N2 - Covering by the Si_3N_4 layer, making the "windows" in the insulator in the wafer parts intended for illumination, selective crystallization of the GaAs layer and additional Zn diffusion for doping this layer.

N3 - Growth of a planar GaAs layer on the germanium substrate, covering by Si_3N_4, making "windows" in the Si_3N_4, selective Zn diffusion.

N4 - Covering with Si_3N_4, making "windows" in Si_3N_4 on the wafer parts intended for illumination, selective growth of a GaAs layer, selective Zn diffusion into the same parts of the wafer.

The first procedure may be used for fabrication of a cascade solar cell in a single technological process. In this case the Zn diffusion into germanium may be carried out in the MOCVD reactor with consequent growth of a second wide-gap gallium arsenide top cell for a multi-junction solar cell. The use of the Si_3N_4 cover in the other procedures ensures protection of the place where the diffusion *p-n* junction comes out to the lateral surface of the solar cell. A similar approach was used for fabrication of the TPV converters based on GaSb.

Fig. 5 presents the dependence of the half-widths of photoluminescence (PL) peaks for layers grown on Ge substrates at different temperatures, and on a GaAs substrate ($T_{growth} = 680^0C$) with the growth rate of about 1 μm/hour. The PL peak halfwidth for the GaAs layer grown on Ge substrates at 630-680^0C are almost in two times wider than those of the layers grown on GaAs substrates.

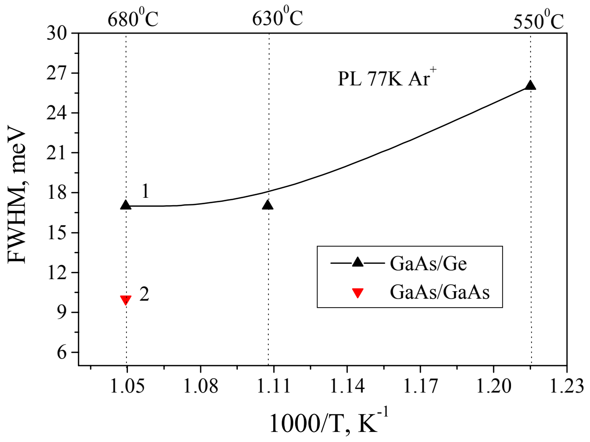

Fig. 5. The dependence of the half-width of PL peaks of GaAs layer grown by MOCVD at different temperatures on Ge (1) and on GaAs at 680^0C (2).

The PL intensity in lowering the growth temperature from 680^0C down to 550^0C decreased by two orders of magnitude, whereas structure surface morphology changed insignificantly. An important factor in this case is that GaAs layer in the structure geometry chosen by us is not a photosensitive layer, but serves to reduce the dislocation density on the GaAs/Ge interface.

Fig. 6 shows spectral photoresponse of a photocell based on the GaAs/Ge heterostructure fabricated by the procedure N3 at the GaAs layer crystallization temperature equal to 550˚C. Rather high internal quantum yield (0.8-0.9) in the wavelength range of 900-1500 nm indicates both a high quality of the GaAs/Ge heterostructure and an optimum profile of doping of the *p*-emitter. The maximum photocurrent density equal to 29.0 mA/cm^2 (T_{growth} GaAs is 630˚C) calculated from the spectral curve of the internal quantum yield in the range of 900-1820 nm is comparable with the photocurrent density, which is achieved in the photocells based on GaAs, measured under AMO spectrum.

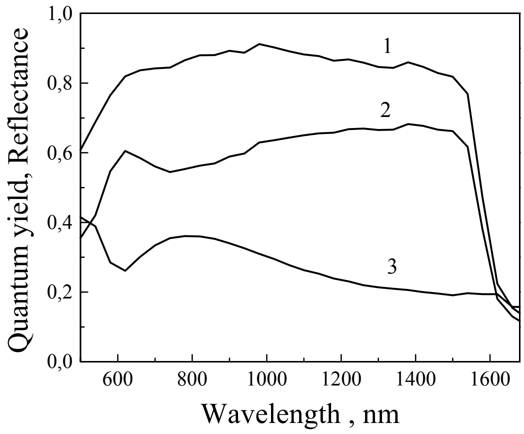

Fig. 6. Internal (1), external (2) spectral responses (at active area) and reflectance (3) of GaAs/Ge PV cells without ARC grown by MOCVD.

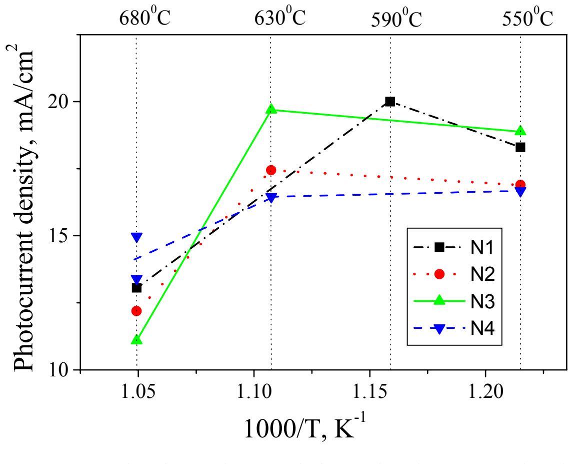

Fig. 7. The dependence of short circuit current density of GaAs/Ge PV cells without ARC versus reciprocal MOCVD growth temperature. Conditions of illumination: λ = 900-1820 nm, AM0 spectrum. Grid fingers shadowing was 6%.

Relying on the spectral photocell photosensitivity, the dependencies of the photocurrent densities (Fig. 7) for all four technological procedures have been obtained in varying the temperature of the wide-gap GaAs window from 680 to 550˚C. It follows from these dependences that the photocell photocurrent density value raises with decreasing the temperature from 680 to 630˚C. The maximum value of V_{oc} = 0.26 V has been also obtained under 1 sun AMO illumination for the cells fabricated by the procedure N3 at the growth temperatures of 630˚C and 550˚C.

It should be noted that using the technological procedure N1 (T_{growth} GaAs is 550˚C) photocells with high photocurrent density of 28.9 mA/cm^2 under AMO illumination calculated from spectrum of internal quantum yield have been fabricated as well. For this reason this approach is promising one too for production of high efficient photocells. Doubtless advantage of the given procedure is that it can be used in growing the GaAs/Ge heterostructure in a single MOCVD process, since it does not include the intermediate stage of covering by a Si_3N_4 layer.

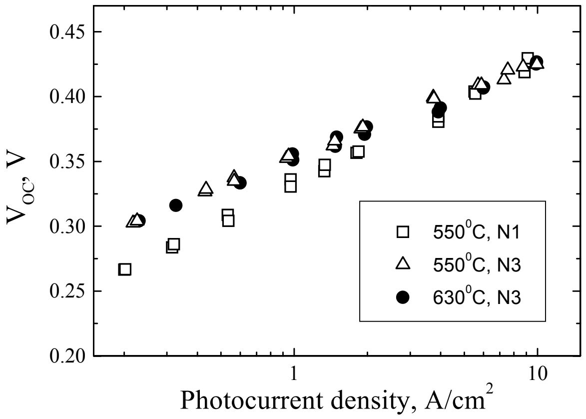

Fig. 8. Open circuit voltage versus photocurrent density for GaAs/Ge PV cells for MOCVD growth temperatures of 630 and 550^{0}C.

V_{OC} raises linearly with photocurrent increase (Fig.8) and achieves a value of 0.42-0.43 V at 10A/cm^2. As we know it is among the highest values of open circuit voltage for GaAs/Ge PV cells measured in such conditions.

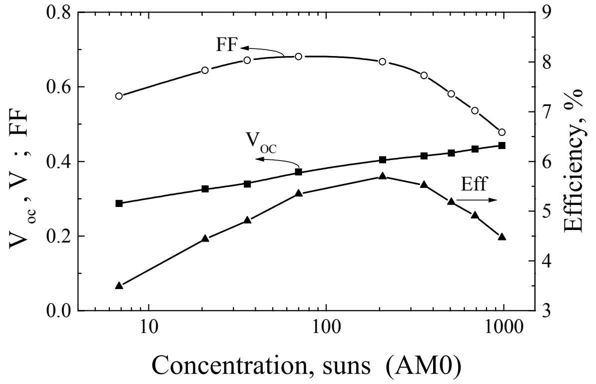

Fig. 9. Fill factor, open circuit voltage and calculated efficiency as a function of sunlight concentration ratio for GaAs/Ge PV cells. Conditions of illuminations: under GaAs "thick" filter and at full AMO spectrum.

Fig.9 demonstrates the behaviour of FF, V_{OC} and efficiency with increasing sunlight concentration. Efficiency calculated from internal quantum yield culminates 5.5-5.7% at 200 suns.

5. CONCLUSION

GaSb based cells with optimized emitter were developed. It allowed increasing efficiencies up to 11% under AM0 spectrum and 19% under a part of AM0 spectrum with λ > 900 nm at photocurrent density of 2-7 A/cm^2.

By means of LPE growth and Zn diffusion, TPV cells based on (*p*-*n*)-InAsSbP/*n*-InAs and (*p*-*n*)-InAs structures were fabricated with the widened photosensitivity in the infrared range of (2.5-3.4) µm.

Combination of the MOCVD technique and Zn diffusion from the gas phase allows fabricating Ge photocells on the base of the GaAs/Ge heterostructure, which is characterized by the higher photocurrent and open circuit voltage values. The photocurrent values achieved in the Ge photocells are close to those obtained in the GaAs solar cells illumination by AM0 sunlight. It ensures a possibility to fabricate the high efficient monolithic tandem solar cells based on GaAs/Ge heterostructures.

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