THERMOPHOTOVOLTAIC CELLS WITH SUB-BANDGAP PHOTON RECIRCULATION

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ABSTRACT: Reflection of non-absorbed sub-bandgap photons from TPV cell allows maximizing the efficiency of a TPV system owing to possible reabsorbtion of these photons in the radiator. Back-surface mirror in the developed Ge and GaSb based cells consists of MgF_2 or Si_3N_4 and Au or Ag layers. Back ohmic contacts Au/Ge/Ni/Au were formed in the holes in MgF_2 layer (with total holes "shadowing" of 3%) and annealed at 400°C. The Ge based TPV cells with back-surface mirror demonstrate reflection of 85% sub-bandgap photons, external quantum yield as high as 0.9-0.95 and extremely high short circuit current of 31.6 mA/cm^2 under sunlight with cut-off at $\lambda < 900$ nm AMO spectrum. The Ge based TPV cells with GaAs wide bandgap window have been fabricated by combination of liquid-phase epitaxy and Zn–diffusion technologies. Efficiency of more than 5% has been received in *p*-GaAs/*p*-Ge/*n*-Ge cells under cut-off ($\lambda < 900$ nm) AM1.5 spectrum at photocurrent densities of 3-20 A/cm^2. The efficiency value of 5.3% at 7 A/cm^2 seems to be the highest one among the published results for Ge-based cells measured in these conditions.
The performance of GaSb TPV cells was improved by optimization of diffused emitter that allowed increasing the short circuit current up to 30 mA/cm^2 for AMO spectrum cut-off at $\lambda < 900$ nm. The deviation of V_{oc} and FF in the 1 cm^2 cells fabricated with the usage of advanced technology is in the following ranges: V_{oc} =0.42-0.45 and FF=0.70-0.72 at photocurrent of 1A. Efficiencies of about 11% under AM0 spectrum and 19% under part of AM0 spectrum with $\lambda > 900$ nm at photocurrent of 2-7 A/cm^2 were achieved in these TPV cells.
Keywords: Germanium – 1: GaSb – 2: Thermophotovoltaic cells - 3

1. INTRODUCTION

Germanium and silicon were the materials at first suggested and applied to thermophotovoltaic conversion of radiation from fuel-fired emitters. However, the first TPV systems based on these materials have not realized their advantages, such as low cost and their commercial availability, because of poor performance received in these cells. Among the III-V compounds, gallium antimonide was the first semiconductor widely used in TPV devices. A reproducible and low-cost Zn-diffusion technology to *n*-GaSb wafers has been developed for fabrication of high efficiency TPV cells, which are now being used for TPV generators [1-8]. Solid solutions InGaAsSb (0.5-0.6 eV) for photoactive layers with GaSb and AlGaAsSb layers as wide bandgap window lattice matched to GaSb have been developed for TPV applications as well [3-10].

Performance of Ge based TPV cells can be improved by growth of GaAs wide bandgap window over Ge wafer and increasing of short circuit current. In this paper we present the results of investigations of Ge based TPV cells with GaAs "window" layer. The performance of GaSb based TPV cells was improved also by optimization of doping profile and thickness of the emitter.

The optimization in a TPV system may implies a choice of the emitter spectrum and a possibility to return a useless part of radiation from receiver back to emitter surface supplying it by an "additional" power. The way to improve the TPV efficiency is to utilize a non-absorbed in the cell part of the emitter spectrum returning it back to the emitter surface where these low-energy photons can be transformed again in the photons of the whole blackbody (graybody) spectrum. The investigation results of TPV cells with back-surface mirrors are presented in this work as well.

2. Ge BASED TPV CELLS

Zn diffusion procedure from vapor phase was applied in order to form *p-n*-junction in Ge wafers. The sizes of cells were varied between 2x2 mm^2 and 10x10 mm^2.

External quantum yield as high as 0.9 (Fig. 1, curve 1) and high short circuit current 29.1 mA/cm^2 with contact shadowing equal to 9% were measured in such Ge cells, illuminated by sunlight with cut-off at $\lambda < 900$ nm under AMO spectrum.

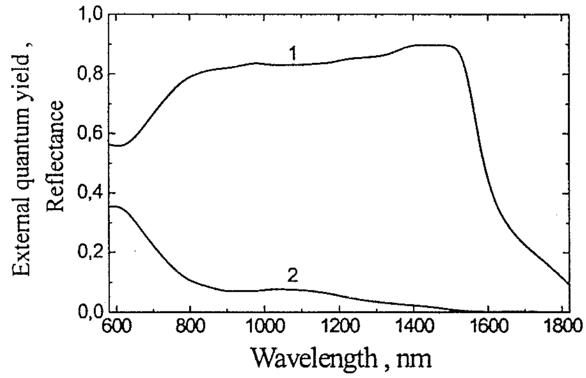

Figure 1: Spectral response (curve 1) and reflectance (2) of *p*-Ge/*n*-Ge TPV cells fabricated by Zn-diffusion.

In comparison with GaSb based TPV cells the worse parameter of Ge TPV cells is open circuit voltage. In order to improve this parameter the technology of LPE growth of thin (0.1μm) GaAs window over Ge wafer has been developed. This growth was carried out at 380 °C from supercooled liquid phase with relatively fast cooling rate of

2 ^{0}C/sec in order to avoid dissolution of Ge substrate. Pb-rich melt was used as a solvent, which ensures a very low solubility of germanium.

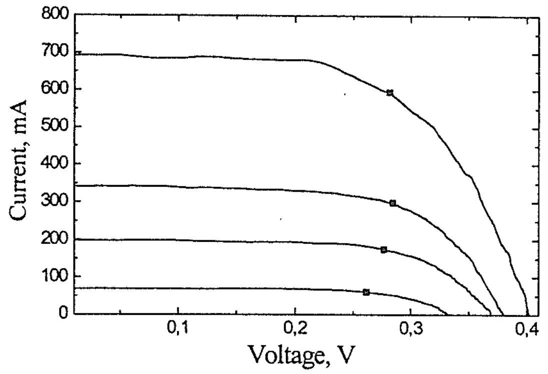

Figure 2: Flash illuminated current-voltage characteristics of a Ge based TPV cells with GaAs wide bandgap window layer.

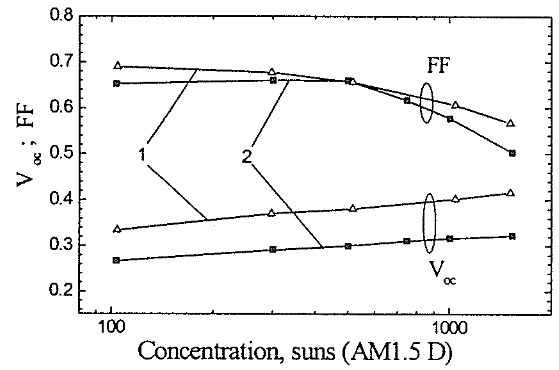

Figure 3: Fill factor and open circuit voltage as a function of sunlight concentration for Ge based TPV cells:
1 - with GaAs wide gap window layer;
2 - without GaAs layer.

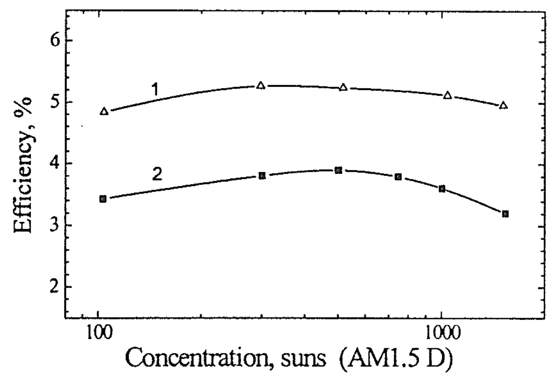

Figure 4: Efficiencies of the Ge TPV cell as a function of concentration sunlight under cut-off at $\lambda < 900$ nm AM1.5D spectrum:
1 - with GaAs window layer;
2 - without GaAs layer.

Fig.2 represents a set of illuminated circuit-voltage curves of *p*-GaAs/*p*-Ge/*n*-Ge TPV cells fabricated by combination of epitaxial and diffusion technologies.

Fig.3 shows the dependencies of fill factor and open circuit voltage versus sunlight concentration for Ge based TPV cells with and without GaAs window. The size of these cells is 2.5×2.5 mm^2. Fig.4 demostrates efficiency of Ge based TPV cells with and without GaAs window layer versus sun concentration.

It is seen that due to improvement of the open circuit voltage an increase of efficiency for Ge based cells from 3.5% (Fig.4, curve 2) up to 5-5.3% (Fig.4, curve 1) at photocurrent densities 3-20 A/cm^2 takes place. To our knowledge it is highest efficiency for Ge-based cells measured in such conditions.

3. GaSb BASED TPV CELLS

Performance improvement of the GaSb based TPV cells was achieved by optimization of the diffused *p*-GaSb emitter.

The diffused *p*-layer parameters are very important taking into account their influence on photocurrent density, sheet resistance and the radiation hardness of the GaSb cells. The diffusion was carried out at the temperature of 460 ^{0}C. The normalized curves of photocurrent (Fig.5) for the cells with different junction depth were obtained from measurement of external quantum efficiency spectra of GaSb diffused TPV cells.

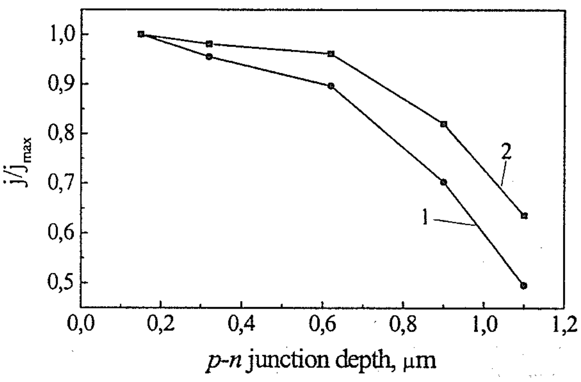

Figure 5: The dependencies of normalized short circuit current density under AM0 spectrum versus the Zn-diffused emitter thickness for GaSb cells:
1 - photocurrent density in the wavelength range from 500 to 1840 nm,
2 -photocurrent density in the wavelength range from 900 to 1840 nm.

It is seen from Fig.5 that the reduction of the photocurrent density with *p*-layer thickness increase for the spectral range from 900 to 1800 nm is less than this reduction for the spectral range of 500-1800 nm. The cells with junction depth 0.6 µm lose only 3.5-4 % of photocurrent for the range of 900-1800 nm, which is the utilized spectral range both for the GaSb tandem solar cells under IR transparent GaAs cells and for the TPV GaSb based cells. The J_{SC} reduction is about 10 % for the cells with junction depth 0.6 μm in comparison with the cells, which have junction depths of 0.1-0.2 μm for the spectral range from 500 to 1800 nm.

There is an additional opportunity to increase the photocurrent by reducing the *p-n*-junction thickness after Zn-diffusion. Precise etching of structure after diffusion allows increasing the photocurrent due to the change both of the junction thickness and of a profile of impurity concentration. The original thickness of *p*-GaSb layer was 300 nm. In order to find an optimum emitter thickness we have etched layers on the depth of 40, 70, 80, 100 and 120 nm by means of anodic oxidation. Such etching decreases the thickness of high doped "dead" surface layer of gallium antimonide (Fig.6).

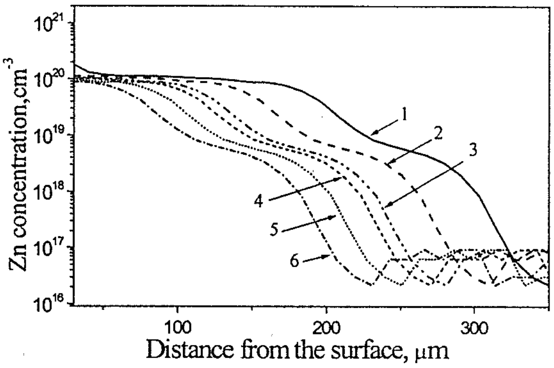

Figure 6: SIMS profiles of Zn concentration after Zn diffusion (curve 1) and after step by step anodic oxidation and etching at final *p-n* junction depths: 0.31 μm (curve 1), 0.26 μm (2), 0.24 μm (3), 0.23 μm (4), 0.21 μm (5) and 0.19 μm (6).

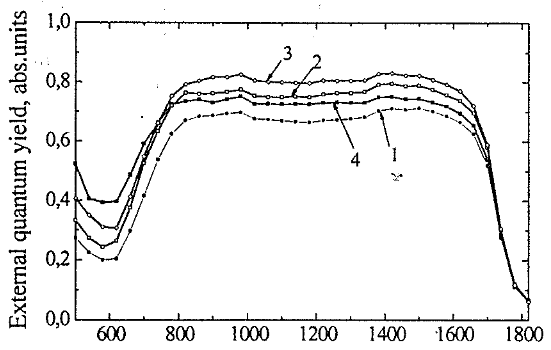

Figure 7: Spectral response (measured on designated illumination area with contact shadowing of 9%) of GaSb diffused (Zn) cells with *p-n* junction depths: 0.31 μm (curve 1), 0.26 μm (2), 0.24 μm (3) and 0.19 μm (4).

Comparison of doping profiles (Fig.6) and spectral characteristics (Fig.7) makes clear that the decrease of high doped surface part of diffused layer from 200 to 90-100 nm leads to the increase of external quantum yield. The further etching leads to a drop of photosensitivity.

Fig.8 demonstrates the dependencies of short current density versus the depth of etched layer. It is seen that optimum post-diffused etching leads to an increase of photocurrent from 26 mA/cm^2 to 30 mA/cm^2 under AM0 spectrum cut-off at $\lambda < 900$ nm. It ensures an additional increase of TPV cells efficiency.

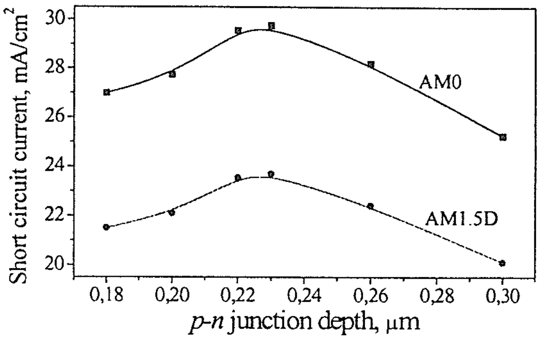

Figure 8: Dependence of short circuit current generated by GaSb TPV diffused (Zn) cells as a function of *p-n* junction depth under AM0 and AM1.5D spectra cut-off at $\lambda < 900$ nm.

4. Ge AND GaSb TPV CELLS WITH BACK-SURFACE MIRROR

Back-surface reflection of non-absorbed sub-bandgap photons from TPV cell allows maximizing the efficiency of a TPV system owing to possible reabsorbtion of these photons in the radiator. Back contacts with increased reflectivity for photons with $h\nu < E_g$ were developed in this work for the cells based on *n*-Ge ($n = 10^{17}$ cm^{-3}, 250 μm thick) and *n*-GaSb ($n = 3 \cdot 10^{17}$ cm^{-3}, 400 μm thick). Back-surface mirror consists of MgF_2 and Au or Ag layers. Back ohmic contacts Au/Ge/Ni/Au are formed in the holes in MgF_2 layer with total holes "shadowing" of 3% and annealed at 400 °C. The front grid contact with shadowing of 6% and ZnS/MgF_2 ARC were fabricated on the front surface and annealed at 250 °C.

The cell reflectance at wavelengths longer than 1.9 μm is about 60% for GaSb cells (Fig. 9, *a*, curve 2) and 82-87% for Ge cells (Fig. 9, *b*, curve 2).

Only 20% reflectance was measured in the GaSb cells with back contact fabricated right to the whole substrate area without intermediate MgF_2 layer (Fig. 9, *a*, curve 3).

External quantum yield as high as 0.9-0.95 (curves 1) and photocurrent densities of 3.8 A/cm^2 on Ge and 4.5 A/cm^2 on GaSb cells were calculated for the photoactive area of the fabricated Ge and GaSb cells under blackbody irradiation with T_{BB} = 1473 K. Open circuit voltage of 0.52 V and FF = 0.68 have been received in GaSb cells at I_{sc} = 4.5 A/cm^2. Efficiency of 11.7% was calculated assuming a radiator temperature T_{BB} = 1473 K and 60% - recirculation of sub-bandgap photons at $\lambda > 1.87$ μm for GaSb cells with measured parameters.

V_{oc} = 0.36 V and FF = 0.6 were received in Ge cells at I_{sc} = 3.8 A/cm^2. Efficiency of 9.8% was estimated for these Ge cells assuming T_{BB} = 1473 K and 85% return efficiency for photons with $\lambda > 1.8$ μm.

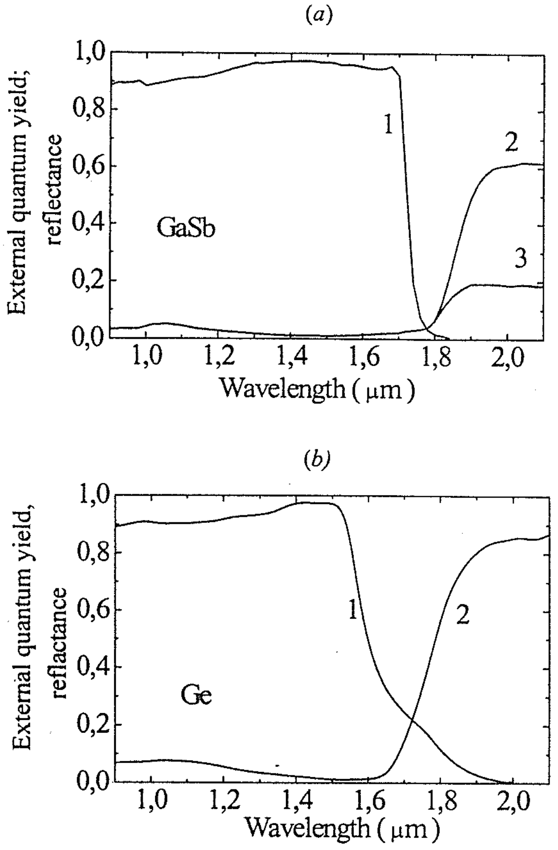

Figure 9: Spectral responses (curves 1) and reflectances (curves 2, 3) for GaSb *(a)* and Ge *(b)* TPV cells with back contact fabricated through the holes in MgF_2 layers (curves 2) and with back contact fabricated right to GaSb substrate without MgF_2 (curve 3).

SUMMARY

The performance of GaSb based TPV cells was improved using the precise anodic etching which results in the increase of the generated current up to 30 mA/cm^2 under AM0 spectrum cut-off at $\lambda < 900$nm.

TPV cells on *p*-GaAs/*p*-Ge/*n*-Ge heterostructures with thin (0.1 μm) GaAs top layers have been fabricated by low-temperature liquid-phase epitaxy and by additional Zn-diffusion into *p*-GaAs-*n*-Ge heterostructure. High external quantum yield in this cell demonstrates low densities of recombination centers on the *p*-GaAs/*p*-Ge interface. Short circuit current of 29.1 mA/cm^2 was measured under sunlight with cut-off at $\lambda < 900$ nm AM0 spectrum. Efficiency of higher than 5% under cut-off ($\lambda < 900$ nm) AM 1.5 D spectrum has been achieved in these *p*-GaAs-*p*-Ge-*n*-Ge TPV cells at photocurrent densities 3-20 A/cm^2.

Reflection coefficient of 85% for sub-bandgap photons was measured in Ge-based TPV cells with back-surface mirror. Efficiency of 9.8% was estimated for these Ge TPV cells assuming black body spectrum at T_{BB} = 1473 K and 85% return efficiency for photons with $\lambda > 1.8$ μm.

Achieved performance in the developed Ge-based TPV cells is a little bit worse in comparison with the best GaSb TPV cells where: V_{oc} = 0.45-0.5 V and FF = 0.7-0.8 at photocurrent densities of 1-5A/cm^2. Nevertheless, taking into account lower cost of Ge-based cells and the higher sub-bandgap photon reflection in the developed Ge-cells with back-surface mirror the conclusion can be made about the perspectives of these Ge TPV cells.

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