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PHYSICS OF SEMICONDUCTOR DEVICES

High-Efficiency GaSb Photocells

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Abstract—High-current solar cells based on gallium antimonide and intended for use in solar modules and systems with solar-spectrum splitting at large solar light concentration ratios, in thermophotovoltaic generators with a high-temperature emitter, and in laser energy converters have been designed and fabricated by the diffusion of zinc from the gas phase. The influence exerted by the thickness of the p^+ diffusion layer on the basic characteristics of the solar cell has been studied. The optimal doping profile and the p–n-junction depth providing a high photovoltaic conversion efficiency at photocurrent densities of up to 100 A cm^{-2} have been determined.

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1. INTRODUCTION

Photovoltaic converters based on gallium antimonide have found wide application in cascade solar cells, e.g., GaAs/GaSb [1–6] or GaInP/GaSb [6], and in thermophotovoltaic (TPV) generators. Also promising is their use in systems with solar-radiation splitting (SRS) [7–10] in which the solar flux is separated by optical filters into spectral ranges for subsequent conversion by spatially separated photovoltaic cells. For example, two optical filters and three single-junction solar cells based on AlGaAs, GaAs, and GaSb were used in a light flux splitting system in [9]. In TPV generators, photovoltaic cells are close (~1–3 cm) to an emitter made of a ceramic or high-melting metals, heated to a high temperature (up to 2000 K) either by solar light concentrated by mirrors or Fresnel lenses [11–13] or by gas burners [14, 15]. GaSb is also a promising material for the development of photovoltaic converters of laser radiation [16]. All the above applications require the development of photovoltaic cells that efficiently operate at photocurrent densities of up to 100 A cm^{-2}. For such high-power photovoltaic converters to be created, it is necessary to provide photocurrent collection from the entire surface of the device at the minimum ohmic loss [17]. The extent to which photovoltaic cells are suitable for operation at high light-flux densities can also be varied by changing the contact grid pattern, width of contact strips, and the spacing between these.

Being comparatively low-cost and simple, the method chosen in the present study for fabricating the photovoltaic-cell structure by diffusion doping from the gas phase is characterized by a high surface concentration of acceptors ($p > 10^{20}$ cm^{-3}) [18–21]. This leads to a shorter minority carrier lifetime in the heavily doped layer and, consequently, to a lower quantum yield (photoresponse) of GaSb photovoltaic cells. We present the results obtained upon post-diffusion precision etching of the surface of the photovoltaic converters fabricated by the diffusion of Zn from the gas phase into a GaSb substrate in order to reduce the thickness of the heavily doped layer. During the process, we changed the p–n junction depth and the zinc concentration distribution profile and studied the effect of the parameters of the structure on the following characteristics of the photovoltaic cell: open-circuit voltage (V_{oc}), fill factor of the load characteristic (FF), photocurrent density (J_{sc}), and light-conversion efficiency.

We developed photovoltaic cells to be used at high incident light intensities in TPV and solar photovoltaic systems, including solar-light splitting modules.

2. EXPERIMENTAL RESULTS

2.1. Fabrication of Photovoltaic Converters Based on GaSb

The device structures of photovoltaic converters based on GaSb are most frequently fabricated using two technological procedures: single- [1, 3, 4, 18, 19] or double-stage diffusion of zinc from the gas phase [2, 6, 10]. The first approach is distinguished by being comparatively low-cost and simple. The advantage of the second procedure is that the p–n junction can be buried under the contacts, which enables the fabrica-

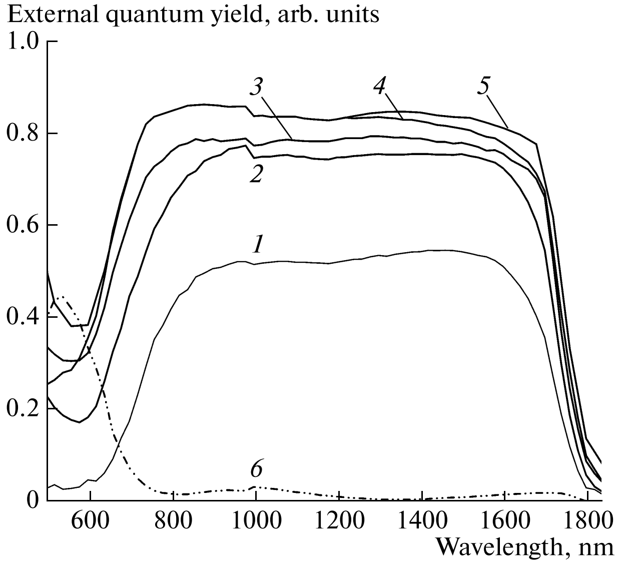

Fig. 1. Spectral characteristics of the external quantum yield of GaSb photovoltaic cells with various *p–n*-junction depths: (*1*) 1.1, (*2*) 0.9, (*3*) 0.62, (*4*) 0.32, and (*5*) 0.14 μm; (*6*) reflectance spectrum of an illuminated GaSb surface with a two-layer ZnS + MgF_2 antireflection coating.

tion of photovoltaic cells that efficiently and reliably operate at a small thickness of the front *p*-GaSb layer in that part of the photovoltaic converter which is free of metallization.

In this study, we formed a complex profile of the *p–n* junction by the two-stage diffusion of Zn through a dielectric mask [2, 6, 10]. The photovoltaic structures under study had a thicker *p*-type layer (d_{p-n} > 1 μm) in the areas under the contacts, compared with the depth of the photosensitive *p–n* junction.

To examine the possibility of improving the parameters of GaSb photovoltaic converters, we varied with precision the diffusion depth on the photosensitive surface by anodic oxidation of the *p* layer, which was followed by selective etching of the oxide in hydrochloric acid. On performing the first diffusion process, we etched the heavily doped photosensitive region of the cell to a depth of up to 560 nm with a step of 80 nm. The averaged anodic oxidation constant of ~2 nm V^{-1} was determined in [18]. The subsequent fabrication stages of GaSb cells (diffusion into the under-contact region and post-growth procedures) remained the same for all photovoltaic converters with different depths of the photosensitive *p–n* junction. The photovoltaic-cell parameters were studied on a pulsed solar simulator at various concentration ratios (up to $K \approx 1000$) or in thermophotovoltaic converters at various temperatures of the tungsten emitter.

2.2. Dependence of the Photoresponse Spectra on the Parameters of GaSb Photovoltaic Converters

The main parameter to be optimized for obtaining the maximum efficiency of solar-light conversion is the *p–n* junction depth d_{p-n}. The diffusion depth and, consequently, the position of the *p–n* junction strongly affect the photocurrent (Fig. 1), radiation hardness, and sheet resistance. Together with the series-resistance losses, the sheet-resistance losses leed to a decrease in the fill factor of the IV characteristic.

The surface concentration of the acceptor impurity in a photovoltaic structure also strongly affects the device parameters. To obtain a high photoresponse, it is necessary to reduce the doping level of the photoactive layer. At the same time, it is preferable to have a heavily doped emitter to decrease the contact and bulk resistances.

The radiation-hardness requirements to space solar cells impose severe limitations on the value of d_{p-n}. Exposure to radiation gives rise to defects in the semiconductor, which is accompanied by a decrease in the lifetime and diffusion length of nonequilibrium carriers. It was shown in [3] that the maximum efficiency for GaSb cells operating in tandem with GaAs photovoltaic converters can be achieved at an emitter thickness of about 0.3 μm and surface hole concentrations of 5×10^{19} cm^{-3} (solar concentration ratio $K > 200$). However, such a decrease in the diffusion-layer thickness may lead in practice to an increase in the leakage current, e.g., upon the annealing of the metallic contacts.

An increase in the thickness of the *p* emitter can make the technological cycle more reliable as regards, e.g., the yield of cells. With increasing *p–n*-junction depth, the bulk resistance of the structure decreases and the fill factor *FF* of the IV characteristic is improved. However, a substantial increase in the thickness of the *p*-GaSb layer impairs the collection efficiency of minority carriers generated near the surface. This fact is confirmed by the experimental photosensitivity spectra of cells with various *p*-region thicknesses, obtained in the present study (Fig. 1). Analysis of these dependences shows that, with increasing *p–n*-junction depth, the external quantum yield decreases in the entire spectral photosensitivity range, especially in its short-wavelength part. At the same time, an increase in the *p* emitter thickness to 0.6 μm leads to an insignificant decrease in the photocurrent. Figure 2 shows how the normalized photocurrent density varies in three spectral ranges, one full ($\Delta\lambda_1$ = 500–1840 nm, curve *1*) and two "reduced" ($\Delta\lambda_2$ = 900–1840 nm and $\Delta\lambda_3$ = 1180–1840 nm). The wavelength range λ_2 (curve *2*) corresponds to the use of GaSb cells in a cascade in a pair with a GaAs photovoltaic cell [4, 5] or in SRS systems combined with two

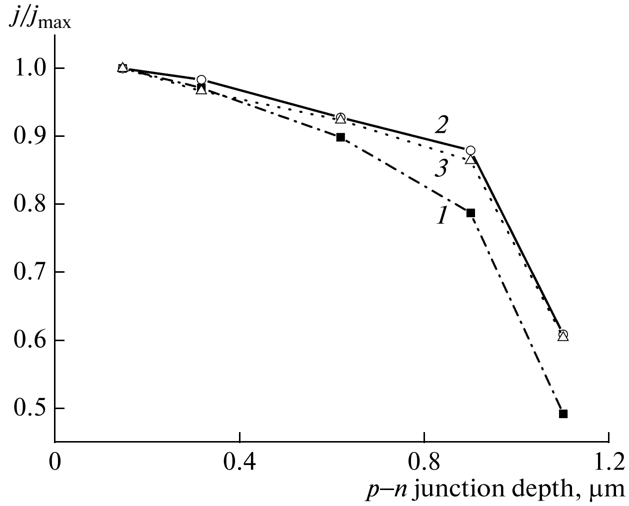

Fig. 2. Dependence of the normalized short-circuit photocurrent density j/j_{max} for structures with various p–n-junction depths: (*1*) $\Delta\lambda_1$ = 500–1840 nm, (*2*) $\Delta\lambda_2$ = 900–1840 nm, and (*3*) $\Delta\lambda_3$ = 1180–1840 nm.

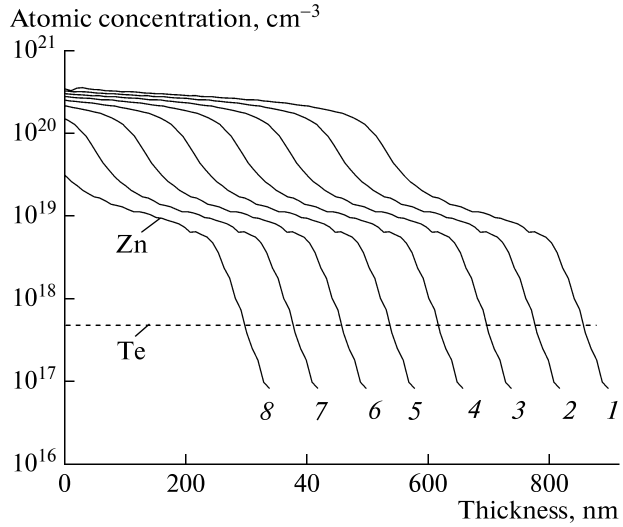

Fig. 3. Distribution of zinc atoms in GaSb with an initial thickness of the front p layer of 850 nm. Thickness of the removed diffusion layer: (*1*) 0, (*2*) 80, (*3*) 160, (*4*) 240, (*5*) 320, (*6*) 400, (*7*) 480, and (*8*) 560 nm.

single-junction photovoltaic converters based on $Al_xGa_{1-x}As$ (x = 0.3–0.35) and GaAs [9]. The $\Delta\lambda_3$ range (curve *3*) corresponds to GaSb cells in a modified SRS system with three dichroic filters [10], into which a fourth photovoltaic converter is introduced (e.g., that based on an InGaAsP/InP or AlGaAsSb/GaSb compound with $E_g \approx$ 1.0–1.1 eV).

Thus, the optimal thickness of the p emitter of the structure may strongly vary with the purpose and operation conditions of the GaSb-based photovoltaic converters. The goal of further studies was to develop a versatile approach to the post-diffusion technology of GaSb photovoltaic-cell structures, which could provide the maximum conversion efficiency for the required p–n junction depth.

2.3. Dependence of the Characteristics of GaSb Photovoltaic Converters on the Diffusion Structure Parameters

The zinc distribution profile in GaSb was measured by dynamic secondary-ion mass spectrometry (SIMS), with $^{133}Cs^+$ as primary ions and $^{133}Cs^{64}Zn^+$ secondary molecular ions recorded. A quantitative analysis was made using the relative-sensitivity coefficients determined on implanted GaSb:Zn standards.

Figure 3 shows the initial zinc distribution profile in GaSb, provided by SIMS for the case of diffusion from the gas phase, and similar profiles obtained upon etching of the structure's emitter. In most of the experiments, the initial p–n junction-depth was 850 nm. One of the advantages of the precision-etching technique is that it can remove the defective heavily doped surface layer, which must reduce the surface-recombination rate. The shape of the curve describing zinc distribution in the device structure also strongly affects the photovoltaic cell parameters. This is so because a change in the doping profile transforms, as a consequence of the decrease in E_g in the heavily doped layer, the built-in electric field created by both the doping and band-gap gradients.

Our experiments demonstrated that a step-by-step (80 nm) decrease in the thickness of the p^+ layer alters

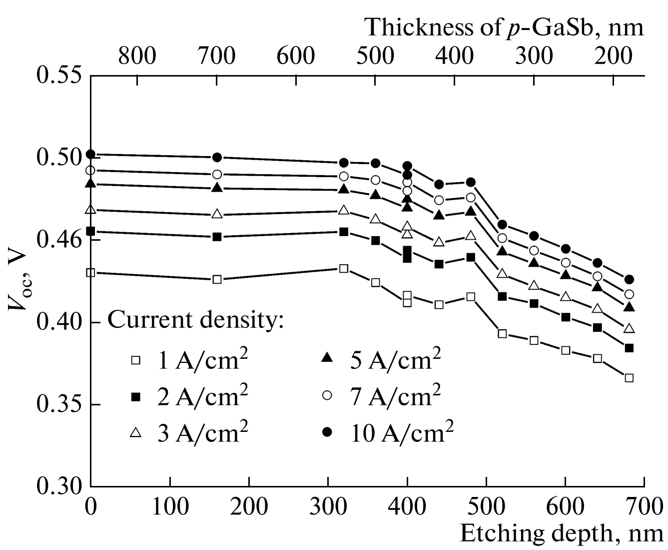

Fig. 4. Open-circuit voltage of a GaSb photovoltaic cell vs. the thickness of the diffusion emitter (upper scale) and the etching depth of the structure (lower scale) at various generated photocurrent densities.

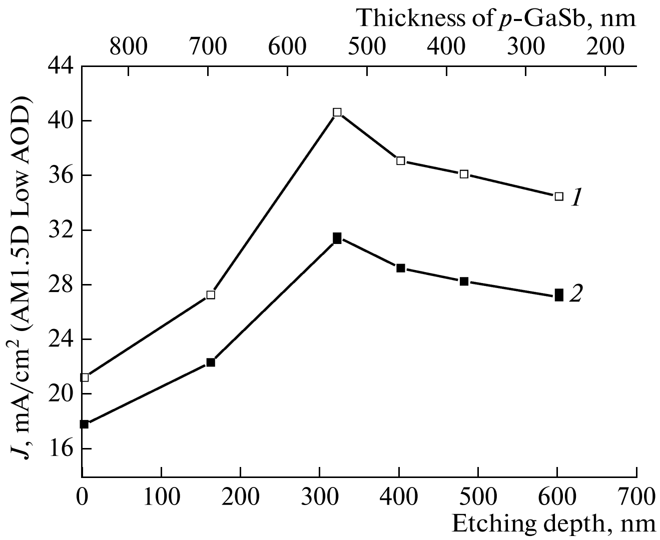

Fig. 5. Photocurrent density vs. the etching depth and emitter thickness: (*1*) for the internal quantum yield and (*2*) for the external quantum yield.

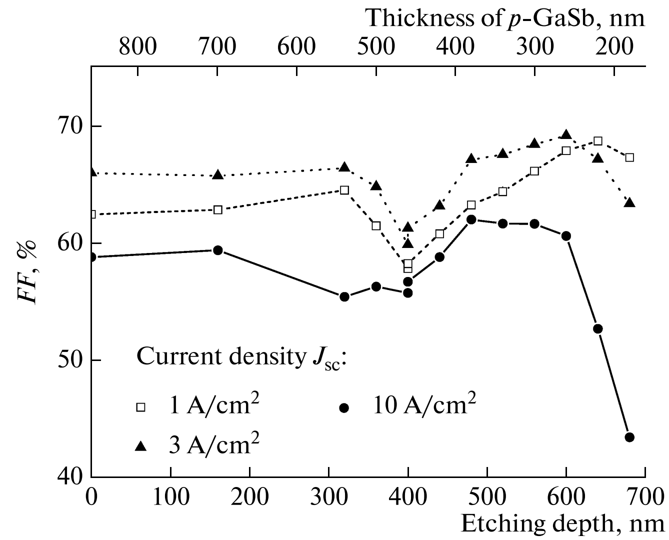

Fig. 6. Fill factor of the current–voltage characteristic vs. the etching depth and diffusion-emitter thickness at different generated photocurrent densities.

the basic characteristics of the photovoltaic converter (Figs. 4–6), which leads to a change in its efficiency. It can be seen in Figs. 7a–7c, which show the resultant dependences of the conversion efficiency on the concentration ratio for the total (Fig. 7a, $\Delta\lambda_1$ = 500–1820 nm) and "reduced" (Figs. 7b and 7c) solar spectra, that the removal of ~320 nm of the structure's emitter corresponds to the highest photovoltaic converter efficiency. From the zinc distribution profiles in Fig. 3 follows that, if the emitter is etched to less than 320 nm, the heavily doped surface layer is removed, but the impurity concentration gradient remains rather large. As the thickness d_{p-n} is reduced further, the concentration gradient falls and, consequently, the built-in field promoting carrier separation becomes weaker. Presumably, this is the reason why the photovoltaic converter efficiency decreases as the thickness of the *p*-GaSb layer is made even smaller.

In [19], the influence exerted by the surface-recombination rate on the quantity $I_{sc}V_{oc}/(I_{sc}V_{oc})_{max}$ (where I_{sc} is the short-circuit current, and V_{oc} is the open-circuit voltage of the photovoltaic converter) was analyzed for five types of diffusion profiles, obtained in different ways. The increase in *FF* upon etching of the emitter to a depth of 500–600 nm, observed in the present study (Fig. 6), may be due to the complete removal of the heavily doped layer (Fig. 3, profile *8*) and to the resulting decrease in the surface-recombination rate to below 5×10^4 cm s^{-1}, according to the estimates made in [19].

The above results are for the photovoltaic converters fabricated on GaSb (100) substrates. The semiconductor ingots were grown by the Czochralski method at Giredmet Institute (Moscow). The wafers were cut and polished at the Ioffe Physical–Technical Institute. Similar studies were carried out for "epi-ready" substrates from Giredmet (Moscow) to confirm the influence exerted by the quality of surface treatment on the effect in which the output characteristics of the photovoltaic converter are improved by post-diffusion etching of the structure. It was demonstrated that the maximum efficiency of the photovoltaic converters (Fig. 8) is also observed at an emitter thickness of 530 nm, obtained upon etching of the structure's emitter to a depth of 320 nm (at an initial *p–n*-junction depth of ~850 nm).

The effect in which the efficiency is improved by etching of the surface layer of the structure was also observed for photovoltaic cells fabricated from "epi-ready" GaSb substrates manufactured by Wafer Technology Ltd (Great Britain). Thus, it can be concluded that the increase in the efficiency of photovoltaic converters due to the etching of their *p* emitter is determined by the post-diffusion change in the *p–n* junction depth and in the zinc distribution profile in the structure, being independent of the substrate manufacturer and specific technological features of their fabrication.

GaSb-based photovoltaic converters with a smaller depth (~500 nm) of the initial diffusion *p–n* junction were studied on GaSb substrates manufactured at Commissariat à l'Energie Atomique, LETI/DOPT (France), and polished at the Ioffe Physical–Technical Institute. It was found that the optimal depth of the post-diffusion etching of the structures with the indicated initial *p–n*-junction depth is 60 nm (Fig. 9).

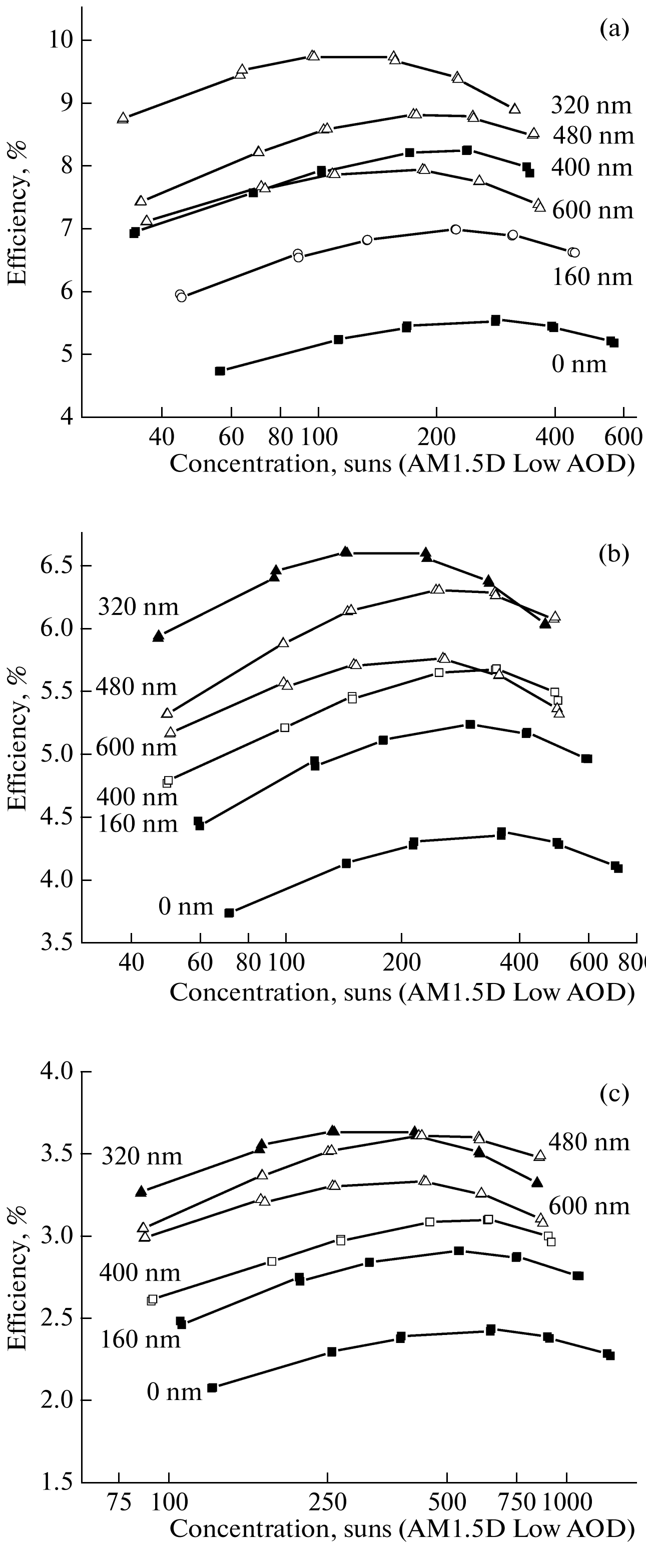

Fig. 7. Efficiency vs. the sunlight concentration ratio at various emitter etching depths for GaSb cells exposed to the following sunlight spectrum bands (AM1.5D): (a) $\Delta\lambda_1$ = 500–1820 nm, (b) $\Delta\lambda_2$ = 900–1820 nm, and (c) $\Delta\lambda_3$ = 1180–1820 nm. GaSb ingot from Giredmet, Moscow; wafer cutting and polishing at the Ioffe Physical–Technical Institute.

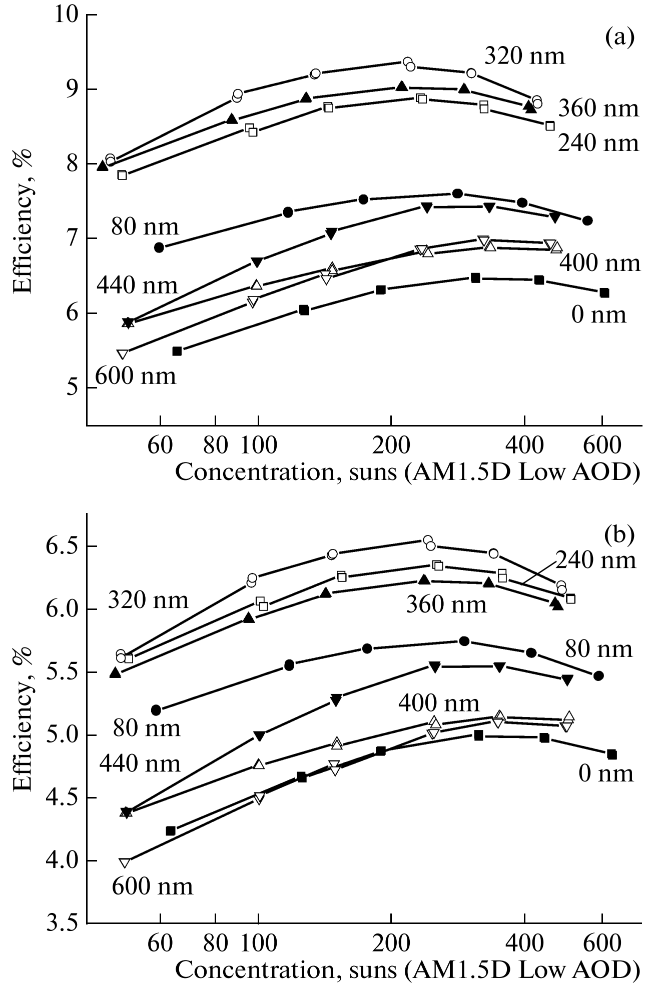

Fig. 8. Efficiency vs. the sunlight concentration ratio at various emitter etching depths for GaSb cells exposed to the following sunlight spectrum bands (AM1.5D): (a) $\Delta\lambda_1$ = 500–1820 nm and (b) $\Delta\lambda_2$ = 900–1820 nm. “Epi-ready” GaSb substrates from Giredmet.

2.4. Testing of the Photovoltaic Converters at Various Tungsten-Emitter Temperatures in TPV Systems

In TPV systems, the thermal radiation is converted into electric power by narrow-gap photovoltaic converters optimized for the conversion of infrared radiation. In this case, the role of the thermal radiation source is played by an emitter heated by concentrated solar light or a gas burner. As the emitter temperature decreases, the specific electric power produced per unit area of the photovoltaic converter decreases. Of particular practical interest are TPV systems heated to the highest (1800–2500 K) temperatures.

GaSb photovoltaic cells intended for use in TPV generators [13, 15] were tested with radiation from a tungsten emitter in the temperature range 1500–2200 K. Figure 10 shows the temperature dependences of the efficiency of GaSb cells without etching

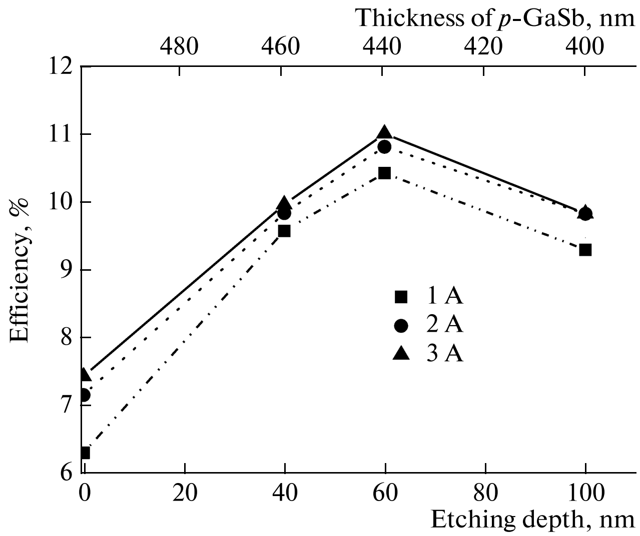

Fig. 9. Efficiency vs. the sunlight concentration ratio for GaSb solar cells (AM1.5D, 1000 W m^{-2}) vs. the emitter etching depth at various generated photocurrent densities. GaSb substrates from LETI/DOPT (France) and Ioffe Physical–Technical Institute.

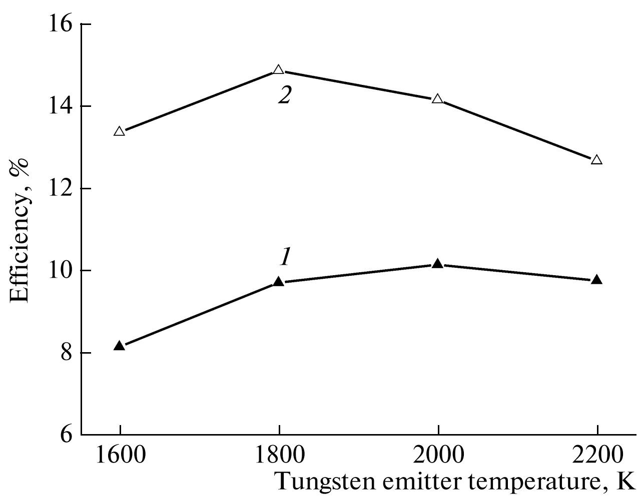

Fig. 10. Efficiency of TPV GaSb cells vs. the tungsten-emitter temperature: (*1*) GaSb structure without thinning of its *p–n* junction and (*2*) structure with a diffusion layer etched to a depth of 320 nm.

of the *p* region (with an initial *p–n*-junction depth of 850 nm) and with optimal etching of the diffusion layer etched to a depth of 320 nm. It can be seen in the figure that the photovoltaic converter efficiency increases from 9.5% (curve *1*) to 15% (curve *2*) at a tungsten-emitter temperature of 1800 K.

3. CONCLUSIONS

Thus, it was found that optimization of the thickness and doping profile of the emitter, formed by the diffusion of zinc from the gas phase and subsequent precision-etching of the structure, markedly improves the characteristics of GaSb photovoltaic converters. These converters can be efficiently used to convert solar light and thermal radiation.

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