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PHYSICS OF SEMICONDUCTOR DEVICES

Photovoltaic Converters Based on GaAs and AlGaAs Epitaxial Layers on GaAs Substrates with Developed Surface Area

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Abstract—MOCVD and LPE technologies of deposition of GaAs and AlGaAs layers onto (100) GaAs substrates with a developed surface area are developed. Porous GaAs layers and surface microprofiles of dendrite and quasi-grating types were fabricated on these substrates. The quality of layers was determined in comparative studies of the surface morphology and X-ray diffraction. Further, photovoltaic converters based on these layers have been devised. The best parameters among the samples under study were attained in photovoltaic converters based on the layers with the dendrite-type microprofile of substrate, which had the most developed area of the working surface and the dislocation density of 10^4 cm^{-2}. In particular, at the wavelength of 0.65 μm, the external quantum efficiency of these photovoltaic converters was 150% higher than in the reference samples produced on a smooth surface.

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New methods of preliminary treatment and protection of the surface of III–V substrates, optimization of parameters of layer epitaxy and postgrowth thermal annealing and other technological techniques have resulted in the development of single-junction and cascade monolithic photovoltaic converters with quite good parameters [1, 2]. Specific attention has also been directed to photovoltaic converters where the initial surface of growth on the substrate has a textured, microprofile structure [3, 4]. As compared to conventional epitaxy of smooth surface, these substrates provide a 30–40% decrease in the internal stress in the layer and an increase in the effective area of the substrate. The latter parameter is especially important because its optimization raises the coefficient of absorption of light by the *p–n* junction, owing to multiple reflections. Further, the use of microprofile substrates offers an additional opportunity for the formation of layers with different conductivity within the surface profile itself. In the last few years, an alternative technology has been developed: epitaxy onto porous III–V substrates, which also have a developed area on the surface and in the near-surface region [5, 6]. It was shown that the use of porous GaAs, InP, and GaSb substrates opens the way for the fabrication of virtually unstressed epitaxial layers with perfect structure, especially if the layers are grown with an additional buffer sublayer. This method appeared to be very promising in the development of high-quality microwave diodes with the Schottky barrier; these diodes have the lowest leakage currents recorded.

Hence, the development of photovoltaic converters on microprofile substrates with developed surface area ("soft" substrates) can offer the following advantages.

(i) Effects of the lattice mismatch between the components of heterojunction and mismatch in the thermal expansion coefficients are reduced owing to relaxation of the stress at the profile of the substrate.

(ii) The absorption of photons by the *p–n* junction is enhanced due to multiple reflections on the profile, which results in a decrease in the optical loss.

However, the use of soft substrates with an active function of separation of electron–hole pairs by the potential barrier localized on the interface leads to the following problems.

(I) An increase in the *p–n* junction area can raise the rate of recombination on the interface and the reverse current of saturation, which will lead to a decrease in the open-circuit voltage of a photovoltaic converter.

(II) In the course of LPE growth, wetting of the microprofile surface by the melt can be incomplete, which will result in a weak adhesion of films to the substrate.

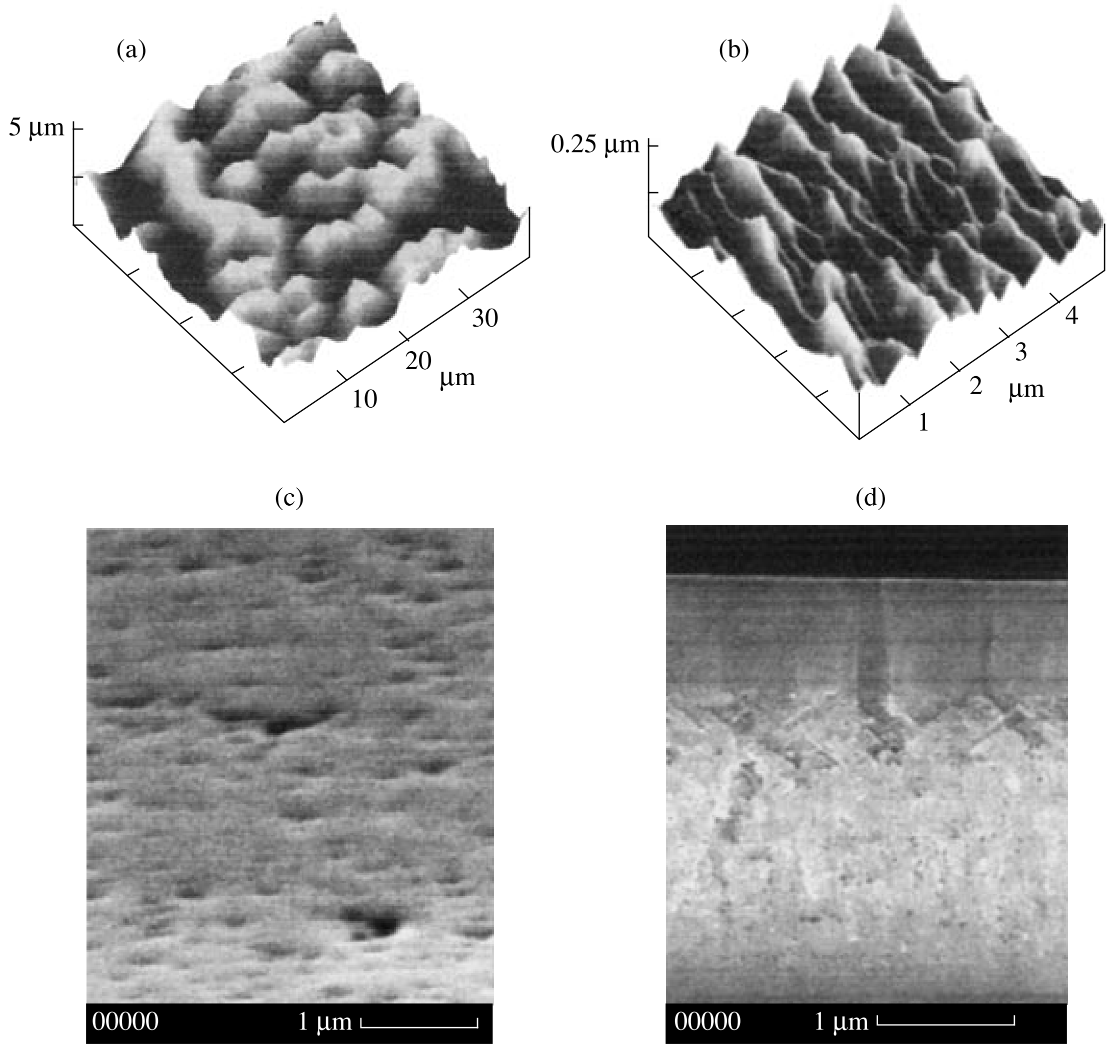

Fig. 1. (a), (b) AFM and (c), (d) SEM images of GaAs microprofile surfaces of (a) dendrite and (b) quasi-grating types; (c) GaAs porous layer; and (d) cross section of the epitaxial layer on a porous GaAs substrate.

The goal of this study was to find the most promising technologies of epitaxy and types of substrates with the developed surface area, in order to improve the parameters of photovoltaic converters. The MOCVD technique was used to grow $Al_xGa_{1-x}As/GaAs$ ($x \approx 0.8$) heterojunctions on various GaAs substrates: standard smooth (reference), porous, and textured, and with two types of the surface microprofile, quasi-grating and dendrite. For comparison, similar heterojunctions were grown by LPE on standard and textured quasi-grating-type substrates. In both cases, (110) n-GaAs substrates doped with tellurium with the concentration of 2×10^{17}–2×10^{18} cm^{-3} were used. Figures 1a and 1b show the surface microprofile of substrates of the dendrite and grating types. These substrates were produced by anisotropic etching in HNO_3 and $2HF : 2H_2SO_4 : 2H_2O_2$ acids, respectively, by the method described in [3, 4]. Porous substrates with a ~10-μm-thick porous layer were produced by electrochemical etching in chloride and bromide aqueous solutions [7]. As can be seen in Fig. 1, the specific scale of nonuniformity for the dendrite-type profile is, in fact, an order of magnitude larger than that for the quasi-grating-type, which, in its turn, is an order of magnitude larger than the scale of nonuniformity of the porous layer surface. Therefore, indeed, these three alternatives cover well a significant range of the surface area development, which favors the solution of the current problem. As will be seen below, this circumstance was especially important in the study of the spectral properties of photovoltaic converters with heterolayers produced by MOCVD.

The quality of the layer structure was estimated in comparative XRD studies using a double-crystal diffractometer (CuK_α-radiation, (311) and (400) reflections). To reveal stresses, we used symmetric (400) and asymmetric (311) reflections, which show the lattice

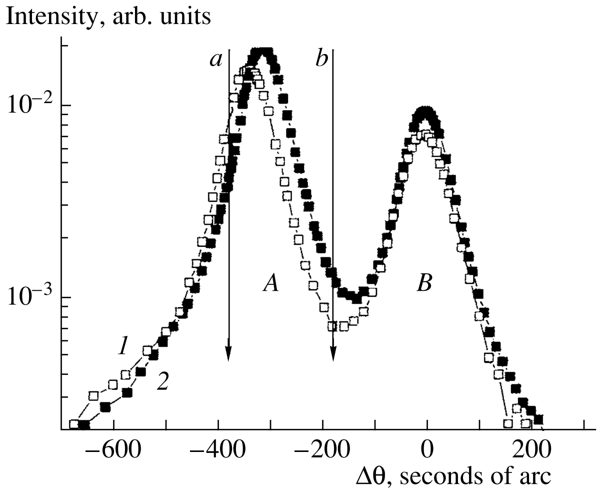

Fig. 2. X-ray rocking curves ((004) reflection, CuK_α radiation) for MOCVD-structures on (*1*) smooth and (*2*) profiled surfaces of GaAs substrate. *A* and *B*, peaks of reflection from $Al_{0.8}Ga_{0.2}As$ epitaxial film and GaAs substrate, respectively; (*a*) and (*b*), peak positions for completely stressed and completely relaxed structures, respectively.

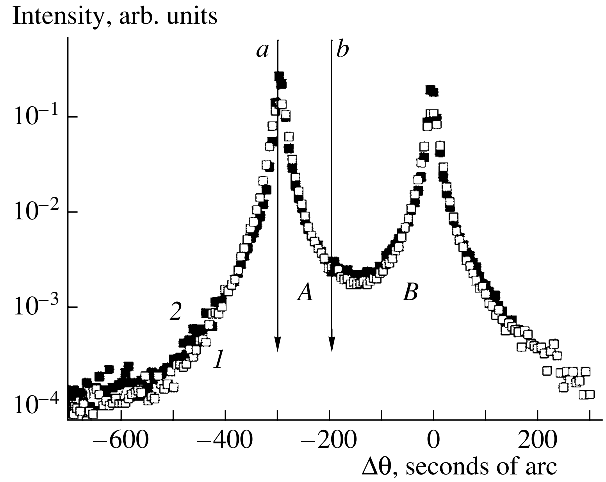

Fig. 3. X-ray rocking curves ((004) reflection, CuK_α radiation) for LPE-structures on (*1*) smooth and (*2*) profiled surfaces of a GaAs substrate. Notations are the same as in Fig. 2.

mismatch for different directions in the unit cell, normal and parallel to interface, respectively. Variations in composition were taken into account on the basis of variation in the intensity of the reflection peaks. These peaks were also analyzed by computer simulation.

The study of structures grown by the developed technology has demonstrated their high quality. As can be seen from atomic force microscopy (AFM) images, the microprofile of textured substrates is partly smoothed during the epitaxy, without a significant decrease in the scale of nonuniformity. At the same time, the initial profile of a porous substrate is nearly completely overgrown by the epitaxial layer (see Fig. 1d).

Figure 2 shows XRD rocking curves of structures grown by MOCVD on textured GaAs. As is well known, the relative intensity of peaks from the film *A* and substrate *B* is determined by the film thickness. In particular, the intensity of peak *A* steadily increases with the film thickness. The thickness of epitaxial films was estimated from the integrated magnitude of peaks. It is independent of the density of structural defects in the film, which allows a rapid and satisfactorily accurate determination of their thickness [8]. It can be also seen from Fig. 2 that, for this epitaxial process, the half-widths of rocking curves for structures with smooth (*1*) and microprofile (*2*) surfaces are close: to each other: 90″ and 87″, respectively. This fact also confirms the high structural quality of the epitaxial layers on the microprofile substrate. Vertical lines *a* and *b* in Fig. 2 show the peak positions for completely stressed and relaxed structures, respectively. The shift of peaks of the rocking curves with respect to the position of line *a* indicates that the strain in the layer is reduced owing to the relaxation of stress. It is noteworthy that the layers on the microprofile surface show more complete relaxation as compared with the layers on the reference smooth surfaces. In both cases, the relaxation is not due to the formation of the misfit dislocations: indeed, one of the mechanisms of broadening of rocking curves for the reflections under study is namely the scattering on these dislocations, and it appears that it is independent of the type of profile.

Figure 3 shows the XRD rocking curves of structures grown by LPE by the method described in [9]. As can be seen, the structures produced by this technique on microprofile substrates seem almost indistinguishable from the structures fabricated on the reference smooth substrates. The comparison of the half-width of rocking curves shows that they are very close to each other. However, these structures appeared to be heavily stressed, virtually in the same way for both types of substrates. The quality of these structures is also high. In particular, the half-width of rocking curves is ~30″, i.e., nearly three times narrower than that for MOCVD-structures. This fact gives us good reasons to believe that the stress in layers can be considerably reduced by optimization of the LPE technology.

Model photovoltaic converters were fabricated from the studied epitaxial heterostructures, and their electrical and photoelectric characteristics were investigated. Figure 4 shows spectra of the external quantum efficiency for several converters fabricated in a single process on substrates with different types of the surface microprofile for a very wide range of the development of the surface area. A qualitative correlation (in terms of an order of magnitude) is observed between the percentage increase in the quantum efficiency and the increase in the area of the working interface. For example, for photons of 0.65 μm wavelength, the quantum efficiency increases by hundreds, tens, and units of percent in samples on the dendrite, quasi-grating, and porous substrates, respectively, as compared to the converter on the smooth substrate. The technology of fabrication of high-efficiency photovoltaic converters presumes that the microprofile is retained in a heteroepitaxial structure after the formation of the *p–n* junction (in our case, this is p^+-$Al_xGa_{1-x}As$/p^+–n–n^+-GaAs). In this situation, the efficiency of a photovoltaic converter will increase not only due to a decrease in the optical loss (the reflectivity), but also due to an increase in the collection of photogenerated carriers, owing to a decrease in the recombination loss at the interface of higher quality. As is well known, anisotropic etching of the GaAs surface provides a high structural quality of the profiled surface which compares well with the initial polished smooth surface [10]. At anisotropic etching, the first to be removed are the most defective regions of the crystal surface, where the etching rate is the highest.

Thus, although the microprofile is somewhat smoothed during epitaxy, the retained microprofile reduces the optical reflectivity. Simulation of the optical and photoelectric characteristics of structures for photovoltaic converters [11] has shown that in this case the p^+-$Al_xGa_{1-x}As$ and p^+-GaAs layers are submicron thick. The use of the MOCVD technique makes it possible to satisfy these conditions, and the maximum effect is reached for the dendrite-type microprofile. In this case, the external quantum efficiency of heteroepitaxial structures with different types of microprofile on the interface correlates with the optical characteristics (the transmission) of layers on microtextured surfaces.

In the case of LPE, it is more difficult to obtain layers, reproducing the microprofile of the substrate, that are sufficiently thin and homogenous across their thickness. Therefore, we used a specific version of LPE with forced cooling in a horizontal reactor with a shifted holder [9]. In this case, $Al_xGa_{1-x}As$ layers of several micrometers in thickness are adequate (e.g., samples LPE-143 and LPE-144, see the table.) However, the microprofile of the working interface is considerably smoothed, which reduces the positive effect of microtexturing. An additional specific feature of the technology of the p^+-$Al_xGa_{1-x}As$/p^+–n^+-GaAs structure of this series is the preliminary deposition of the p^+-$Al_xGa_{1-x}As$ layer onto the textured n^+–n^+-GaAs ($n = 2 \times 10^{17}$ cm^{-3}) substrate. The emitter p^+-GaAs layer is formed later, owing to diffusion of Zn during epitaxy. As can be seen from the table, the best parameters of photovoltaic converters were obtained for thinner layers (sample LPE-145), where the initial profile of the substrate is better retained. It is noteworthy that, under similar conditions of epitaxy, the efficiency of converters on the dendrite-type substrates is higher, as can be seen from the comparison of data for samples LPE-143 and LPE-147. It is necessary to note also that for these samples the optimal composition parameters were found to be $x = 0.74$ and 0.6, respectively.

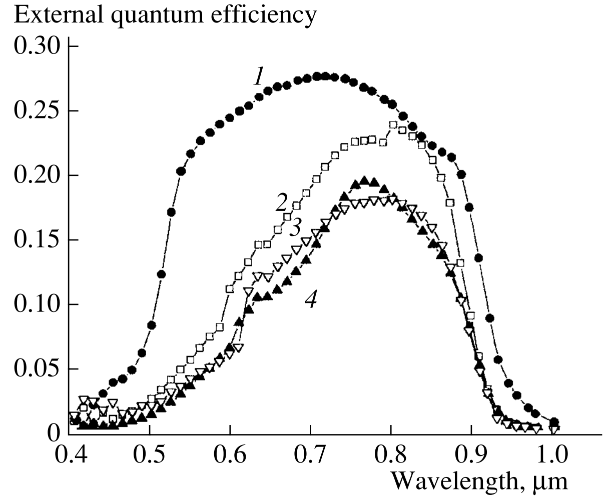

Fig. 4. Spectra of the external quantum efficiency of MOCVD structures with the surface profile: (*1*) dendrite-type, (*2*) quasi-grating, (*3*) porous layer, and (*4*) initial smooth.

Figure 5 shows the forward current–voltage (*I–V*) characteristics in the dark, recorded using photovoltaic converters based on LPE-produced structures. These data

Parameters of photovoltaic converters based on structures produced by LPE. The source of illumination was a simulator of extra-atmospheric sunlight spectrum (AM0 radiation)

Sample no.	Profile	$Al_xGa_{1-x}As$ layer		J_{sc}, mA cm^{-2}	V_{oc}, mV	*FF*	η, %
		x	thickness, μm				
LPE-144	Smooth	0.75	3.5	15.63	869	0.289	2.88
LPE-143	Quasi-grating	0.74	3.5	8.39	827	0.740	3.76
LPE-145	Quasi-grating	0.47	<1	14.44	976	0.795	8.21
LPE-147	Dendrite	0.6	3.6	21.8	624	0.499	5.1

Note: J_{sc} is the short-circuit current density; V_{oc}, the open-circuit voltage; *FF*, the filling factor (the product of maximum current by voltage, reduced to the product of J_{sc} by V_{oc}); and η, the power efficiency.

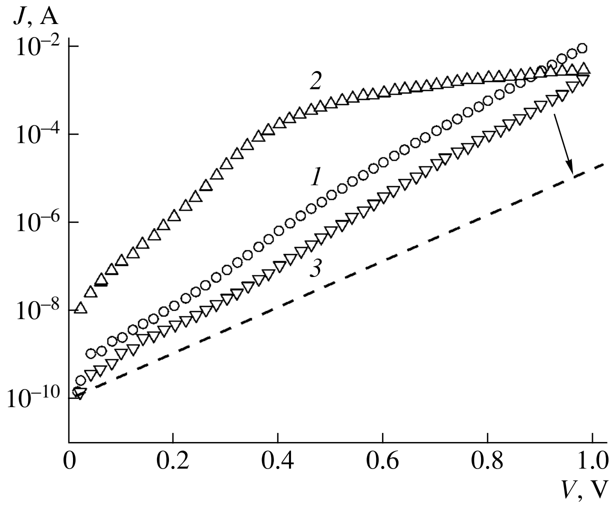

Fig. 5. Forward *I–V* characteristics in the dark for photovoltaic converters based on LPE-structures on: (*2*) smooth surface, sample LPE-144; (*1*) and (*3*), microprofile substrates of quasi-grating type, samples LPE-143 and LPE-145, respectively. Dashed line, the simulated characteristic for a sample on porous substrate with the dislocation density in the layer of 10^3 cm^{-2}. The arrow indicates the shift of this line as the technology of epitaxy is optimized.

also indicate that structures on microtextured substrates have higher structural quality than those on reference smooth substrates. The simulation of *I–V* characteristics using analytic dependences [12], which take into account the basic mechanisms of current flow (diffusion, recombination in the depleted layer, tunneling along the dislocations threading through the space charge region, and ohmic shunting) allowed us to reveal the structure-dependent tunneling component of current and estimate the density of dislocations ρ_d. For structures with smooth interface, e.g., LPE-144, we obtain $\rho_d \approx (1–2) \times 10^5$ cm^{-2}, and for microprofiles LPE-143 and LPE-145 $\rho_d \approx (1–2) \times 10^4$ cm^{-2}. As was shown in [13], the density of dislocations in epitaxial layers on porous substrates can be reduced to 10^2–10^3 cm^{-2}. Based on this possibility and the model [12], we have simulated the *I–V* characteristic for a photovoltaic converter on a porous substrate, which is shown in Fig. 5. It must be taken into account that the achievement of large gain in the external quantum efficiency seems problematic, because, as mentioned above, the area of the working interface of these structures is not developed.

Thus, the results of X-ray studies of structure of the device LPE-layers on textured and porous substrates, and the parameters of photovoltaic converters based on these layers are indicative of the potential of this technology. The best parameters of converters are obtained for thinner layers p^+-$Al_xGa_{1-x}As$ and p^+-GaAs (sample LPE-145), where the initial profile of the substrate is better retained. However, at smaller duration of LPE process (and diffusion of the acceptor impurity), the properties of an $Al_xGa_{1-x}As$ layer can be inconsistent with the demanded parameters in the value of x, as well as in the layer thickness and homogeneity, so further optimization of the microprofile parameters and epitaxy process are necessary.

Based on the obtained data, we can advance the following conclusions.

(i) Epitaxial growth of thin $Al_xGa_{1-x}As$ layers on a "soft" GaAs substrate (porous, microprofile) opens the way for the fabrication of an $Al_xGa_{1-x}As$/GaAs heterosystem with its structure parameters highly competitive with systems on smooth chemically polished substrates. Further optimization of the epitaxy and diffusion processes is necessary to improve the parameters of photovoltaic converters and raise the structure yield.

(ii) The MOCVD process and diffusion of impurity from the gas phase seem more promising than LPE for the production of photovoltaic converters with high parameters. However, LPE can be used to reduce the cost in the mass production of converters with high area of illumination.

(iii) Texturing of the active interface of the heterojunction (*p–n* junction) reduces the optical loss without a significant increase in the saturation current. For the emission of the AM0 solar simulator, the efficiency of conversion by the $Al_xGa_{1-x}As$/GaAs photovoltaic converter can be raised by 10–20%.

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