Monolith GaAsP/Si dual-junction solar cells grown by MBE

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Abstract. The growth of monolith GaAsP/Si dual-junction solar cells on Si substrates by molecular-beam epitaxy is demonstrated. The technological method for the formation of a highly doped tunnel p+/n+ junction was developed. An obvious increase in the value of the open-circuit voltage indicating the contribution of the top-junction in the total open-circuit voltage monolithic dual-junction solar cells was found.

1. Introduction

Currently, among renewable energy sources, photovoltaic conversion of solar energy is recognized as the most promising. One of the main indicators of all solar cells is their conversion efficiency - a value that shows what percentage of the power of solar radiation incident on the Earth can be converted into electrical energy. There are various ways to increase the energy conversion efficiency of solar cells and the use of monolithic nanoheterostructures is one of the most successful areas of their development. An important advantage of monolithic nanoheterostructural solar cells based on A₃B₅ compounds is their ability to efficiently convert concentrated solar radiation, which reduces the consumption of semiconductor materials in proportion to the concentration ratio of solar radiation and significantly reduces the cost per watt of solar energy. [1]

Nevertheless, the modern approach to instrument making is based on reducing the cost of precursors (substrates, materials used for growth, etc.), proven technology of cheap and mass technological production, and integration of several devices on a single chip, which leads to the transition to a technological platform for manufacturing devices based on Si. In the last decade, significant progress has been made in the development of a technological platform for the manufacture of passive devices, such as filters, waveguides, splitters, adders and photovoltaic converters, based on Si for integrated photonics. Integration of active devices remains a very difficult task. Currently, active photonic devices on a silicon platform are produced by bonding, either a chip-on-chip, or on the basis of an A₃B₅ substrate. [2-5] However, in this case the part of III-V materials is lost during substrate removal.

Direct epitaxy on silicon overcomes these problems, but in most cases there are problems with the mismatch of the lattice parameter and differences in thermal expansion coefficients. [6-8] Part of the problem can be solved by thick relaxation layers (buffer layers), using active regions of the quantum dots to reduce threading dislocations [9] or using complex compositions of materials, such as Ga (N, As, P), which provide the lattice parameter matching. [10]

The density of threading dislocations in the direct growth of III-V on Si can be significantly reduced through the use of selective growth and geometric effects in nanostructured materials. [11, 12] In this case it is possible to obtain high quality crystalline material, but there are limitations in the accuracy and the size of the device. Though, for all the above-mentioned methods, separate
manufacturing techniques for III-V and silicon materials are required, which cannot be performed on the same equipment due to cross-contamination.

Here we report on the growth of monolith GaAsP/Si dual-junction solar cells on Si substrates by molecular-beam epitaxy and the study of their properties.

2. Experiment

Epitaxial growth of the studied samples was carried out on MBE set up with cracker-type solid-state sources of arsenic and phosphorus and molecular sources of gallium, aluminum, indium, as well as effusion sources of silicon and beryllium alloying materials. To eliminate the problem associated with the formation of antiphase domains during the growth of III–V compounds on silicon, we used the vicinal surface of the silicon substrate with miscut angle of 4° towards [110] direction. Prior to the growth, the silicon substrates were subjected to a cycle of chemical treatment by the Shiraki method [13]. During the course of chemical treatment, the native oxide overlayer was removed from the substrate surface and a passivating layer of non-stoichiometric SiO₂ was formed. Subsequent annealing of the substrate in the MBE growth chamber at 850°C was performed to remove the passivation layer and the remaining traces of chemical compounds.

To form the n-GaP nucleating layer on a p- Si(100) substrate, we used the migration-enhanced epitaxy (MEE) technique [14]. After the formation of the n-GaP nucleating layer, the n-GaP buffer layer was formed by the standard MBE method. The state of the surface during epitaxy was controlled by the method of reflected high-energy electron diffraction (RHEED).

Figure 1 shows a schematic representation of a monolithic nanoheterostructure GaAsP/Si dual-junction solar cells grown on a silicon substrate. A series connection of photocells in a monolithic GaAsP/Si SC was carried out by means of a p⁺/n⁺ tunnel junction (Fig. 1). Usually, p⁺/n⁺ tunnel junction is present p–n junction with a high doping level corresponding to the semiconductor degeneration state, and is specially formed between stages to ensure low ohmic losses between the “upper” and “lower” elements of a dual-junction SC. The quality of the interfaces of the obtained samples was investigated using a Supra25 Zeiss electron scanning microscope.

![Figure 1](image-url)

**Figure 1.** Schematic representation of a monolithic nanoheterostructure GaAsP/Si dual-junction solar cells.

3. Results and discussion

The formation of nucleating and buffer GaP layers with thicknesses of 10–20 and 150–200 nm, respectively, on a silicon substrate leads in the end to the appearance of a distinct streaky RHEED...
pattern and a comparatively smooth surface of the resulting crystal. The optimal epitaxial temperatures of the GaP nucleating layer are 350°C. In this case, a dashed-line RHEED pattern is formed and no transition to 3D growth occurs (Fig. 2a). During growth of the GaP buffer layer, the substrate temperature gradually increases to 620°C. As the GaP buffer layer grows, the GaP surface becomes smoother and the structure of the RHEED pattern changes from dashed-line to that of the streaky type (Fig. 2b).

Figure 2(a, b). RHEED pattern of the GaP surface during the growth of a nucleating layer on a silicon substrate.

After the buffer layer a GaAs$_x$P$_{1-x}$:Si gradient layer was grown. The $x$ changed from 0.1 to 0.3, is necessary for the transition from the silicon lattice parameter to the lattice parameter of the upper GaAs$_{0.3}$P$_{0.7}$ sub-element. For the formation of a highly doped p'/n+ tunnel junction, a technological method for doping of GaAs$_{0.3}$P$_{0.7}$ layers by silicon to a carrier concentration of more than $1 \times 10^{19}$ cm$^{-3}$ was developed. This technological method consisted in reducing the temperature of the substrate and special δ-Si inserts into the GaAs$_{0.3}$P$_{0.7}$ layers. During the growth of the heavily doped GaAs$_{0.3}$P$_{0.7}$:Be layer in the tunnel junction, the substrate temperature was reduced to 550°C to create a carrier concentration above $1 \times 10^{19}$ cm$^{-3}$ and prevent beryllium segregation on the layer surface.

Figure 3 shows a cross-sectional scanning electron microscope (SEM) image of a monolithic nanoheterostructure GaAsP/Si dual-junction solar cells. Despite the fact that the RHEED pattern of the layer has a streaky structure, an undulating microprofile is clearly seen on the surface. We found the formation of cones which can be associated with the annihilation of antiphase domains. They were formed at the Si/GaP heterointerface and were penetrated into the GaP layer to a depth of up to 100 nm (Fig. 3 circumscribed areas). Visible defects in the upper part of the nanoheterostructure GaAsP/Si dual-junction solar cells are not observed.

A theoretical calculation of the quantum efficiency spectrum of the SC obtained as the upper subelement of a dual-junction SC on a silicon substrate was performed. The simulated structure is a p-i-n junction with an active i-layer of GaPAs 400 nm thick and heavily doped n- and p-type plates. The calculation was carried out in the AFORS-HET 2.5 free software environment [http://www.hmi.de/bereiche/SE/SE1/projects/aSi/Si/AFORS-HET], which automatically solves the Poisson and continuity equations in the one-dimensional case using drift and diffusion currents, which allows you to build a band diagram and extract the carrier concentration and other important parameters within the structure. Figure 4 shows the spectra of external quantum efficiency (QE) at a reflection of 30%, depending on the value of the lifetime in the i-layer, which was varied by introducing effective nonradiative recombination centers in it. The best agreement with experimental data is achieved at a lifetime of $5 \times 10^{-12}$ s. Obviously, this is a low value; therefore, the use of i-GaPAs layer for photoconverting applications is justified, since it allows to achieve a better collection of carriers compared with doped. However, according to calculations, even for lifetimes longer than 1 ns, the integral and maximum QE in the absence of reflection does not reach high values. This leads to calculated short-circuit current values of several mA/cm², which is insufficient for use in high-performance monolithic SCs.
Figure 3. SEM image of a monolithic nanoheterostructure GaAsP/Si dual-junction solar cells. Circumscribed areas show the annihilation of APDs. Scale bar corresponds to 200 nm.

The current-voltage characteristic of the monolith GaAsP/Si dual-junction solar cell without an antireflection coating is shown in Figure 5. This SC has the following characteristics measured under AM1.5 illumination: open circuit voltage - 0.9 V; short circuit current - 0.8 mA/cm²; fill factor (FF) - 27.8%. Since monolithic dual-junction SC are a series connection of two current sources, the total current flowing in the external circuit will be equal to the minimum current generated by each p–n junction. The current value of the SC will be the highest when the magnitudes of the photocurrents of the upper and lower elements are consistent. Such coordination is achieved by selecting the width of the optical gap and the thickness of each of the i-layers. Therefore, a non-high short-circuit current value is determined by the upper element of the GaPAs/Si dual-junction solar cell and corresponds to the calculated data. In addition, a noticeable increase in the open circuit voltage value, compared with the value for a GaP/Si-based photocell (insert Fig. 5), indicates of the contribution of the upper element to the total open circuit voltage of a monolithic nanoheterostructure GaAsP/Si dual-junction solar cells. Thus, the technological method used to form a tunnel junction allows one to synthesize the monolith GaAsP/Si dual-junction solar cell on a silicon substrate by the MBE method.

Figure 4. Experimental and calculated (for different values of the lifetime) spectra of the external quantum efficiency of the upper subcell with the active i-GaPAs layer.
Figure 5. The current-voltage characteristic of monolith dual-junction GaPAs/Si solar cell. The inset shows the current-voltage characteristic of the GaP/Si photovoltaic cell.

4. Conclusion
The formation of initial GaP layers was performed by migration-enhanced epitaxy (MEE) method. The technological method for the formation of a highly doped tunnel p'/n'-junction have been developed and optimized to reach low ohmic losses between top and bottom sub-elements of dual-junction solar cells. The scanning electron microscopy studies of the samples obtained demonstrate that single crystalline GaPAs/Si layers were formed. The investigation of current-voltage characteristics exhibited the formation of dual p-n junction. Furthermore an evident increase in the value of the open-circuit voltage indicating the contribution of the top-junction in the total open-circuit voltage monolithic dual-junction solar cells was demonstrated.

Acknowledgments
The work was partially supported by the grant of Minobrnauki № 16.9789.2017/BCh and Skoltech (agreement № 3663-MRA).

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