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Post-growth technology of multi-junction photovoltaic converters based on A3B5 heterostructures

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Investigation and development of the post-growth technology for fabricating multi-junction photovoltaic converters based on GaInP/GaInAs/Ge heterostructure has been carried out. Antireflection coating, ohmic contacts and mesa-structure forming stages have been reviewed. The technology of n^+-GaAs contact layer etching with the help of plasma-chemical, liquid and ion-beam etching has been investigated. Antireflection coefficient of radiation from the heterostructure with TiO_x/SiO_2 (x close to 2) antireflection coating surface was less then 3% in wavelength range 450−850 nm. The value of contact resistance for n- and p-type conductivity was $3 \cdot 10^{-5}-3 \cdot 10^{-6}\,\Omega\mathrm{cm}^2$, the decrease of photosensitive region shading degree at increased bus-bar conductivity has been archived. The mesa-structure surface current leakage decreased to the value of 10^{-9} A at voltage less then 1 V.

Keywords: photovoltaic converters, ohmic contacts, antireflection coating, mesa-structure

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Introduction

The research into concentrator photovoltaics is crucial for the energy industry, since this technology offers an environmentally friendly and efficient way of conversion of solar radiation to electric energy. The widespread interest in multi-junction photovoltaic converters (PVCs) stems from their high efficiency: a value of 47% was demonstrated for six multi-junction A^3B^5 cells in conversion of concentrated solar radiation (AM 1,5) [1–3].

Post-growth processing of heterostructures, which involves the formation of an antireflective coating, Ohmic contacts, and a separating mesa-structure [4,5], is one of the key stages of PVC fabrication. Research and development works on individual processing stages allow one to reduce optical and ohmic losses in conversion of solar radiation and enhance the efficiency and durability of PVCs.

1. GaInP/GaInAs/Ge heterostructure

Research and development of the post-growth technology of formation of multi-junction PVCs was carried out based on a GaInP/GaInAs/Ge heterostructure with an upper GaInP subelement, a middle GaInAs subelement, a Bragg reflector, a buffer GaInAs layer, and a lower Ge subelement. This heterostructure was grown on a p-type germanium substrate (Fig. 1). The growth of the upper GaInP subelement ends with the formation of a wide-bandgap $Al_{0.52}In_{0.48}P$ window and an n^+-GaAs contact layer needed to reduce the contact resistance of the frontal Ohmic contact.

2. Post-growth technology of PVC formation

The post-growth PVC processing sequence includes photolithography needed to create the intended topology pattern in a photoresist, formation of an antireflective coating and Ohmic contacts, and etching of the separating mesa-structure. The sequence of processing procedures is defined with account for the composition of the heterostructure and the device topology. Optimizing the processing sequence,

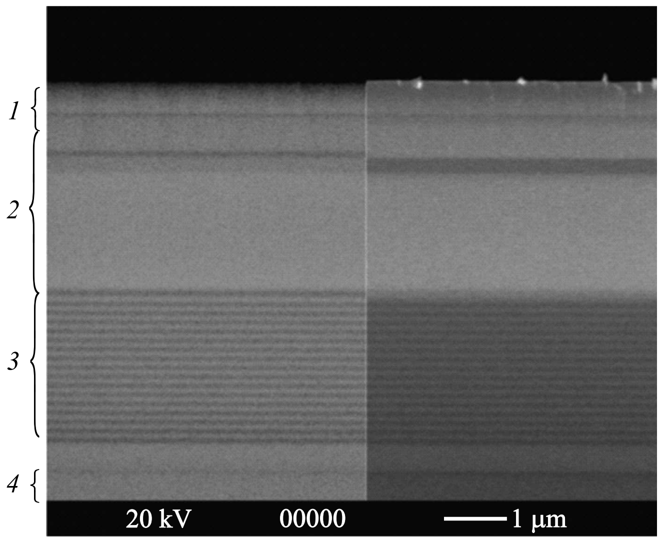

Figure 1. Cleaved layers of the GaInP/GaInAs/Ge heterostructure imaged with a scanning electron microscope: *1* — GaInP subelement, *2* — GaInAs subelement, *3* — Bragg reflector, *4* — Ge subelement.

one enhances the technological effectiveness and reliability of post-growth processing. In the present study, we worked out and optimized the processing sequence with the following key stages:

— etching of the n^+-GaAs contact layer outside the region of the frontal Ohmic contact and formation of an antireflective coating (ARC) by deposition of TiO_x/SiO_2 layers through a photoresist mask;

— formation of the frontal Ohmic contact by evaporation of Au(Ge)/Ni/Au layers through a photoresist mask;

— formation of the continuous rear Ohmic contact by evaporation of Ag(Mn)/Ni/Au layers;

— electrochemical thickening of Ohmic contacts;

— formation of a separating mesa-structure by etching of layers of the heterostructure and the substrate.

3. Antireflective coating

An ARC on the photosensitive PVC region reduces the coefficient of reflection of solar radiation. Multilayer coatings based, e.g., on TiO_x (with x close to 2), SiO_2, Si_3N_4 layers [6], are used to minimize the reflection coefficient in a wide interval of the solar spectrum. The state of the PVC surface affects the ARC parameters. Studies into the PVC surface preparation were carried out in order to achieve fine characteristics of adhesion of the ARC to the semiconductor structure surface with the minimum coefficient of reflection of solar radiation.

In order to expose the photosensitive region of the heterostructure, local etching of the n^+-GaAs contact layer outside the region of the frontal Ohmic contact is performed selectively to the wide-bandgap $Al_{0.52}In_{0.48}P$ window. The processes of plasma-chemical, wet chemical, and ion-beam etching of the contact layer of the heterostructure were examined.

Selective plasma-chemical etching of the n^+-GaAs contact layer to the $Al_{0.52}In_{0.48}P$ stop layer is performed in BCl_3 and SF_6 plasma. The key advantage of plasma-chemical etching is the high accuracy with which the PVC topology is specified. This accuracy is attributable to the process anisotropy and the lack of lateral etching under the photoresist mask. The damaged layer is proposed to be removed after plasma-chemical etching by subjecting the surface to wet chemical etching to a depth lower than 100 nm with highly diluted compositions based on hydrogen peroxide with the addition of orthophosphoric or sulphuric acids.

In the case of wet chemical etching of the n^+-GaAs contact layer, etchants based on citric acid and hydrogen peroxide (or ammonia and hydrogen peroxide) are highly selective to the $Al_{0.52}In_{0.48}P$ stop layer. However, owing to the isotropy of properties of wet chemical etching, the n^+-GaAs contact layer is etched partially under the photoresist region. As a result, the PVC topology is specified less accurately.

In addition, wet chemical etching is specific in that a natural oxide layer forms on the heterostructure surface after chemical treatment and washing with deionized water. The thickness and the composition of this layer depend on the composition of the etchant used. The quality of the heterostructure surface may be enhanced by performing additional ion-beam etching in Ar environment to clean the structure and remove the oxide layer prior to the ARC deposition. Different rates of etching (V) of the surface of the wide-bandgap $Al_{0.52}In_{0.48}P$ window and different surface states were obtained by varying the accelerating voltage (U): $U = 100$ V, $V = 0.3$ Å/s; $U = 300$ V, $V = 0.8$ Å/s.

The influence of etching parameters on the coefficient of reflection of solar radiation from the heterostructure surface with an ARC based on TiO_x/SiO_2 layers was studied. It was found that the etchant composition and the technical regime of etching do not exert a considerable influence on the coefficient of reflection of solar radiation in the operating wavelength range of the PVC. The reflection coefficient increases by 0.1% at $U = 100$ V and by 0.2% at $U = 300$ V if additional ion processing is performed prior to the ARC deposition. However, surface cleaning has a considerable effect on the ARC adhesion to the heterostructure surface, and a less than a percent increase in the reflection coefficient may be neglected.

The following methods of preparation of the photosensitive PVC region are the most advanced and optimal in terms of reproduction of the given topology, rate of etching of the n^+-GaAs contact layer, and ARC adhesion:

— plasma-chemical etching with the damaged layer removed using a highly diluted etchant based on hydrogen peroxide and sulphuric acid;

— wet chemical etching with a highly diluted etchant based on $NH_4OH + H_2O_2$ with additional ion-beam processing at $U = 100$ V.

A reflection coefficient below 3% in the 450−850 nm wavelength interval (the sensitivity region of the upper two subelements) was achieved with both methods (Fig. 2). It

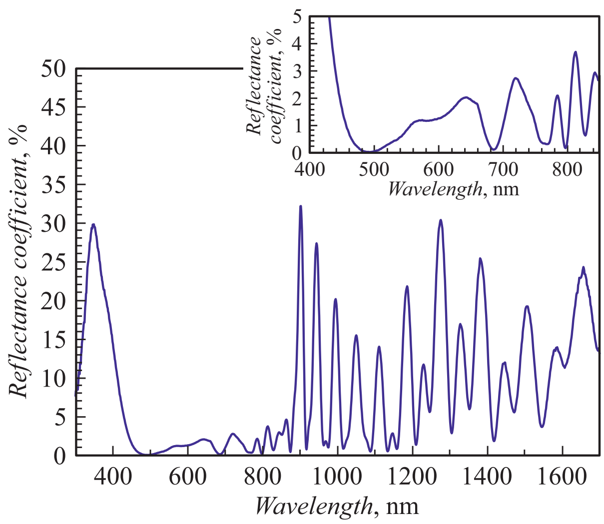

Figure 2. Spectral characteristic of the coefficient of reflection of solar radiation from the GaInP/GaInAs/Ge heterostructure surface with the TiO_x/SiO_2 ARC.

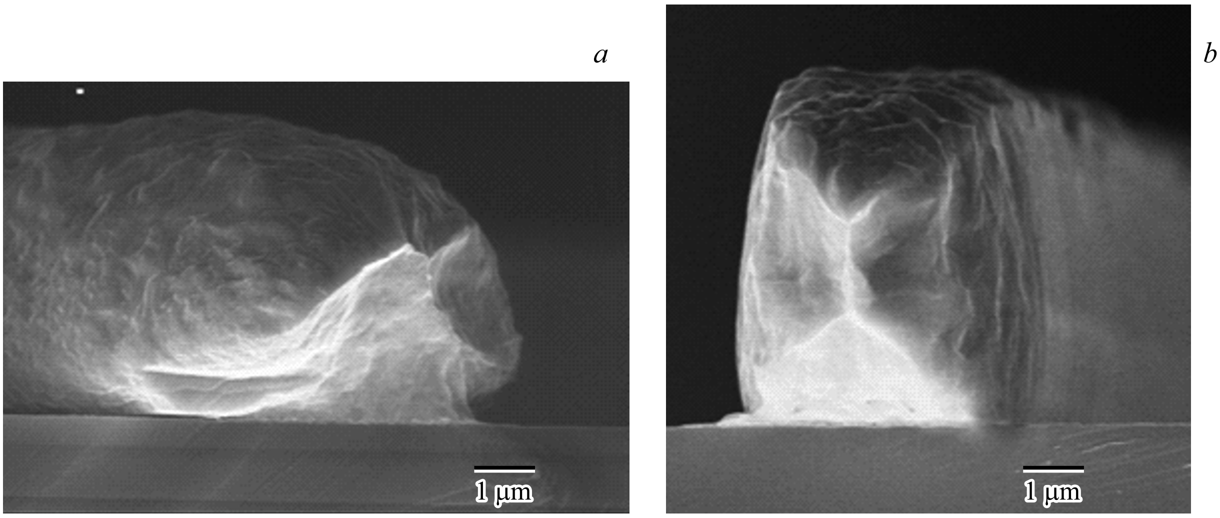

Figure 3. Cleave of contact bus-bars after the electrochemical deposition of gold (*a*) and silver (*b*) imaged with a scanning electron microscope.

should be noted that the germanium subelement is sensitive within the 950−1600 nm wavelength interval. Since the current produced by this subelement is 20−30% stronger than the current of the upper two subelements [7], the essential requirements regarding the suppression of reflection are imposed in the 350−950 nm wavelength range.

4. Ohmic contacts

Development and optimization of the technology of formation of Ohmic contacts of a PVC help reduce the Ohmic losses in conversion of solar radiation into electric energy [8–10]. If the concentration of solar radiation is above 500×, the photocurrent density exceeds 10 A/cm^2. In order to improve the efficiency of PVC operation in these conditions, one needs to reduce the contact resistivity and raise the electrical conductivity of contact bus-bars, thus enhancing the current collection and heat removal.

A contact system based on Au(Ge)/Ni/Au layers used as the frontal Ohmic contact allows one to reduce the contact resistivity to the n^+-GaAs layer to $3-5 \cdot 10^{-6}\,\Omega\,\mathrm{cm}^2$. A rear Ohmic contact based on Ag(Mn)/Ni/Au layers to a *p*-type germanium substrate provides a resistivity lower than $3-5 \cdot 10^{-5}\,\Omega\,\mathrm{cm}^2$. The technology of electrochemical growth of Ohmic contacts by deposition of gold- or silver-based contact materials [11] is used to raise the electrical conductivity of contact bus-bars.

The growth of Ohmic contacts is performed through the photoresist mask. The formation of vertical walls of the mask profile is optimal for the fabrication of contact bus-bars maximizing the electric conductivity of a contact and minimizing the optical losses due to shading of the photosensitive PVC region.

The cyanide gold-plating solution is a widely used electrolyte for gold deposition. Gold is deposited at a temperature of 50−60°C. If the indicated plating solution is used, the mask decays under the influence of elevated temperature and (CN^-) ions, resulting in debonding between the photoresist and the semiconductor surface and spreading of gold into the photosensitive PVC region. Optical losses increase with the width of contact bus-bars. In order to suppress the contact outgrowth, one may perform the deposition of gold through a double-layer mask with a dielectric sublayer and a photoresist layer. Insulation of the conducting surface of the semiconductor heterostructure reduces the voltage across the semiconductor/mask/electrolyte heterointerface; detachment of the photoresist from the semiconductor surface is prevented, and gold is deposited in line with the mask profile (Fig. 3, *a*).

The ferricyanide silver-plating solution may be used in electrochemical deposition of silver. This electrolyte does not damage the photoresist mask, which is attributable to the high plasticity of silver and the specifics of the deposition process at room temperature. The electrochemical deposition of silver is performed in accordance with the photoresist mask profile and provides an opportunity to form contact bus-bars with a vertical side wall of an increased thickness (4−7 μm) without increasing the degree of shading of the photosensitive PVC region (Fig. 3, *b*). The obtained topology and the low specific resistivity of silver $(0.015-0.016\,\Omega\,\mathrm{mm}^2/\mathrm{m})$ enhance the conductivity of contacts with minimal optical shading losses.

5. Mesa-structure

The mesa-structure is formed to divide the entire heterostructure area into PVC chips. The multilayer semiconductor heterostructure based on GaInP/GaInAs/Ge consists of thin layers with different physical and chemical properties. This presents certain difficulties in the process of etching.

In the present study, isotropic and anisotropic methods of heterostructure etching are examined.

Wet chemical etching and electrochemical etching are isotropic methods. Their drawback is lateral etching of the heterostructure under the photoresist mask, which complicates potentially the process of passivation of the mesa side wall with a dielectric coating. The differences in rates of etching of layers with different chemical properties may result in overetching in thin layers. Therefore, new etchants need to be developed when the composition of the heterostructure changes. However, a wide spectrum of available chemical agents provides an opportunity to develop the technology of mesa formation for various heterostructures [12].

The proposed two-stage procedure is a technologically advanced method for etching of layers of the GaInP/GaInAs/Ge heterostructure. At the first stage, selective etching of GaInP/GaInAs layers to the germanium substrate is performed with an etchant containing $K_2Cr_2O_7$, HBr, H_3PO_4; at the second stage, Ge is etched. Different methods for etching of the germanium substrate were examined:

— with a highly diluted etchant based on hydrobromic acid and hydrogen peroxide;

— with an etchant based on orthophosphoric acid and hydrogen peroxide;

— electrochemical etching with a weakly alkaline electrolyte based on glycerine.

The highly diluted etchant (HBr, H_2O_2) provides a very low etching rate (below 0.1 μm/min) and is very sensitive to the presence of metal particles in the solution. The process is thus technologically inappropriate and unreliable, since overetching in individual layers of the heterostructure is possible. The etching rate for the (H_3PO_4, H_2O_2) etchant and the weakly alkaline electrolyte based on glycerine is on the order of 1 μm/min; defects on the side surface of the mesa are lacking.

The method of plasma-chemical etching is anisotropic [13,14]. Layers of the GaInP/GaInAs/Ge heterostructure were etched to form the separating mesa-structure in boron trichloride (BCl_3) plasma using an STE ICP 200e (SemiTEq) plasma-chemical etching setup in accordance with the inductively coupled plasma – reactive ion etching (ICP/RIE) technology with subsequent removal of the damaged layer by wet chemical etching.

Dark current-voltage curves were measured with an accuracy of measurement of the dark current of 10^{-12} A to analyze the influence of mesa-structure formation techniques on the PVC parameters (Fig. 4). In the case of wet chemical etching, the leak current is below 10^{-9} A at voltages lower than 1 V (Fig. 4, curve *2*), but the parameters vary greatly over the heterostructure area. When we switch to plasma-chemical etching, the leak current increases slightly (Fig. 4, curve *1*) due to the formation of the damaged layer. If this layer is removed, the leak current drops below 10^{-9} A at voltages lower than 1 V (Fig. 4, curve *3*).

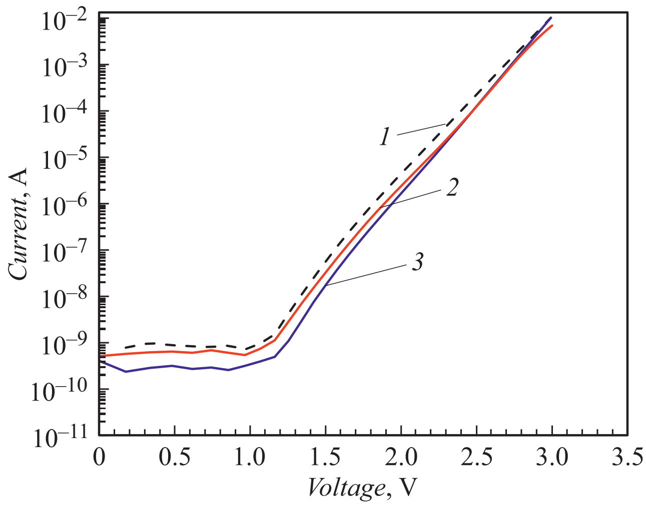

Figure 4. Dark current-voltage curve of the PVC after the formation of the separating mesa: *1* — plasma-chemical etching, *2* — wet chemical etching, *3* — plasma-chemical etching + removal of the damaged layer.

Conclusion

The results of research and development works on different stages of the post-growth processing of A^3B^5 heterostructures were presented. The stages of ARC formation, including etching of the n^+-GaAs contact layer and cleaning of the surface prior to the deposition of TiO_x/SiO_2 layers, were examined. The coefficient of reflection of solar radiation from the heterostructure surface with the ARC deposited onto it was reduced to lower than 3% in the wavelength interval of 450−850 nm. A method for the formation of thickened Ohmic contacts based on silver with a low degree of shading of the photosensitive PVC region and an enhanced conductivity of contact bus-bars was developed as a result of research into contact systems. A method for the formation of a separating mesa-structure by wet chemical etching and plasma-chemical etching was developed. The leak current was reduced to lower than 10^{-9} A at voltages below 1 V.

Conflict of interest

The authors declare that they have no conflict of interest.

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