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Plasmachemical etching in postgrowth technology of photovoltaic converters

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Investigation of the heterostructure plasmachemical etching technology for fabricating multi-junction photovoltaic converters has been carried out. The dividing mesa-structure forming stage at different etching regimes and subsequent disturbed layer removing by liquid chemical treatment has been reviewed. The influence of mesa etching methods on cells photovoltaic characteristics has been investigated. Developed was the technology of photovoltaic converters fabrication with low current leakage values less than 10^{-9} A at voltage less then 1 V with high resistance to degradation.

Keywords: photovoltaic converter, heterostructure, plasmachemical etching, mesa-structure.

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Introduction

Concentrator multi-junction photovoltaic converters (PVCs) offer the highest efficiency of conversion of solar radiation [1–4]. The record-high efficiency value for six-junction PVCs is 47% with 140x concentration of solar radiation (AM 1.5) [2].

Three-junction PVCs based on a GaInP/Ga(In)As/Ge heterostructure, which includes more than 20 layers with different physical and chemical properties, are the most widespread [3–6]. The post-growth treatment of these heterostructures in PVC fabrication is a fairly labor-consuming process. The results of research and development works on the prost-growth technology of PVC fabrication reveal the possibility to reduce Ohmic and optical losses by optimizing the regimes of fabrication of Ohmic contacts and antireflective coatings and reduce current leakage through the use of a dividing mesa-structure [7].

The present study is focused on the process of formation of a dividing mesa in fabrication of a PVC based on a GaInP/Ga(In)As/Ge heterostructure by plasmachemical etching performed in a STE ICP 200e setup (SemiTEq). The regimes of etching and treatment of heterostructures were optimized. The influence of process parameters on the electrical PVC characteristics was estimated.

1. Parameters of plasmachemical etching

The division of a wafer into chips is one of the stages of post-growth treatment of heterostructures in PVC fabrication. The etching of GaInP/Ga(In)As heterostructure layers and the germanium substrate to a depth of $10-15\,\mu$m, which exceeds the thickness of heterostructure layers by a factor of 2, is proposed in order to protect the end face of $p-n$ junctions from physical impact in the process of dicing and thus reduce the perimeter current leakage. Inductively coupled plasma reactive-ion etching (ICP/RIE) in a flow of BCl_3 working gas is a widely used method of plasmachemical etching for mesa-structure formation [8,9].

The process of plasmachemical etching involves a number of technological parameters that affect the rates of etching of individual heterostructure layers, the resistance of the photoresist mask used to protect the photosensitive area of elements, and the surface quality of the mesa-structure as a whole. A series of experiments with different technological parameters of plasmachemical etching being varied were performed in order to optimize the process conditions.

The key process parameters are as follows: pressure P in the chamber, inductively coupled plasma (ICP) power, bias (RIE) power, bias voltage U, and temperature T of the table on which the heterostructure is positioned. These parameters affect the rate of etching of GaInP/Ga(In)As heterostructure layers (V_{3j}), the rate of etching of the germanium substrate (V_{Ge}), and the selectivity of etching of the structure over the protective mask (S). The etching selectivity parameter quantifies the difference between the rates of etching of layers of the structure and the mask and thus characterizes the level of protection of the structure in the process of mesa formation.

Several independent experiments with a series of parameters being fixed and one parameter (changing from one experiment to the other) being varied were carried out to estimate the influence of a large set of parameters on the technological process. The following fixed values were set to estimate the influence of pressure in the chamber on the etching process: ICP = 600 W, RIE = 100 W (Fig. 1). The bias voltage at the substrate holder electrode is a characteristic of the process of plasmachemical etching that defines the energy and the flux of ions incident onto the heterostructure surface. The table temperature

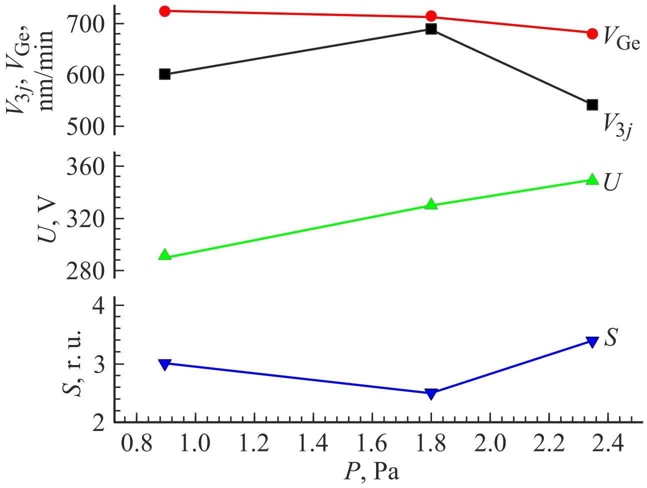

Figure 1. Dependence of the heterostructure etching rate (V_{3j}, V_{Ge}), the bias voltage (U), and the selectivity (S) on pressure in the chamber.

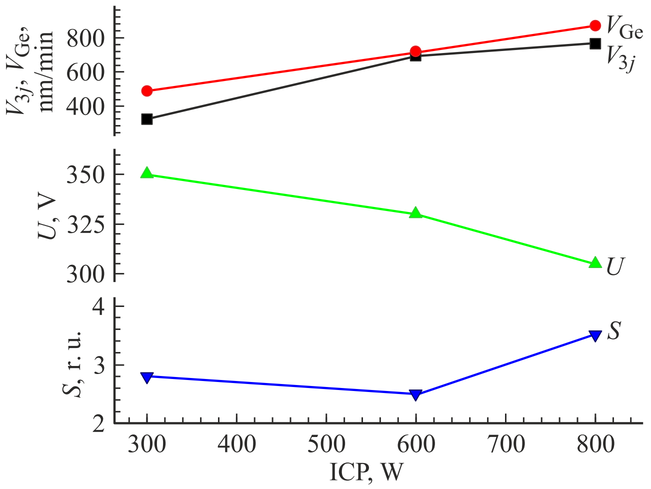

Figure 2. Dependence of the heterostructure etching rate (V_{3j}, V_{Ge}), the bias voltage (U), and the selectivity (S) on inductively coupled plasma (ICP) power.

is kept constant at ~ 10°C, which provides cooling of the treated heterostructure and enhances the resistance of the photoresist mask.

The experimental results revealed that the rates of etching of heterostructure layers and the germanium substrate become similar at a pressure of ~ 1.8 Pa in the chamber, thus providing an opportunity to form an even lateral mesa surface. The selectivity of etching of the structure over the protective mask varies from 2.5 to 3.5. This guarantees a mask resistance sufficient to form a dividing mesa with a depth of 10–15 μm.

The following fixed values were set to estimate the influence of inductively coupled plasma (ICP) power on the etching process: RIE = 100 W, $P = 1.8$ Pa (Fig. 2). The etching rates become similar at ICP = 600 W.

The following fixed values were set to estimate the influence of bias power (RIE) on the etching process: ICP = 800 W, $P = 1.8$ Pa (Fig. 3). The etching rates become similar at RIE = 100 W.

The optimum parameters of plasmachemical etching of the GaInP/Ga(In)As/Ge heterostructure in a flow of BCl_3 working gas were determined as a result of this study: inductively coupled plasma power ICP = 600 W, bias power RIE = 100 W, bias voltage $U = 290$ V, pressure in the chamber $P = 1.8$ Pa, and table temperature $T = 10$°C. These process parameters set close rates of etching of the germanium substrate and GaInP/Ga(In)As heterostructure layers, which differ in their physical and chemical properties, and thus provide an opportunity to form a dividing mesa-structure with an even lateral surface. Since a high-quality etching surface without defects forms in this case, the current leakage along the lateral mesa surface at the sites of emergence of p–n junctions is also reduced (Fig. 4, *a*). The

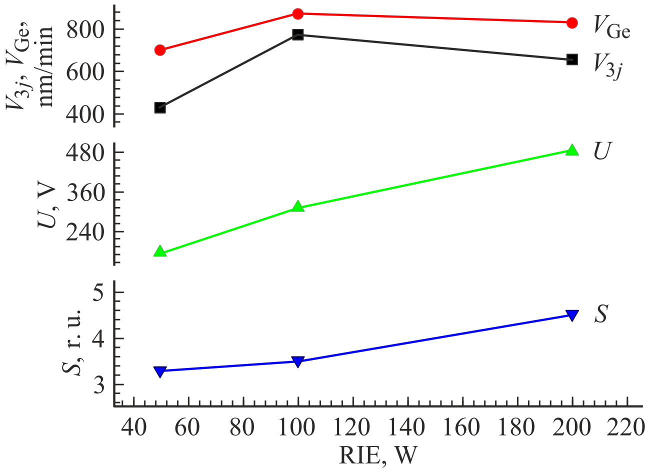

Figure 3. Dependence of the heterostructure etching rate (V_{3j}, V_{Ge}), the bias voltage (U), and the selectivity (S) on bias power (RIE).

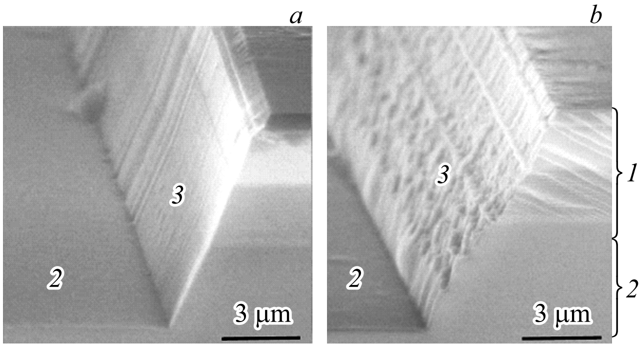

Figure 4. Cleaved mesa-structure imaged with a scanning electron microscope after plasmachemical etching (*a*) and after removal of the damaged layer in the process of etching in H_2SO_4:H_2O_2:H_2O for 100 nm (*b*). *1* — GaInP/Ga(In)As heterostructure, *2* — germanium substrate, *3* — lateral surface of the mesa-structure.

selectivity of etching of structure layers over the protective photoresist mask ($S > 2.5$) ensures reliable protection of the photosensitive PVC area and reduces the probability of emergence of defects and overetching of the structure.

2. Removal of the damaged layer

A damaged layer, which may compromise the operation of elements in aggressive environmental conditions (specifically, in the case of strong temperature gradients and high humidity), forms in the process of plasmachemical etching of heterostructure layers. The mesa-structure surface was subjected to wet chemical etching to a depth of 30–100 nm in order to remove the damaged layer in the present study.

The methods of mesa etching with a number of highly diluted etching solutions of orthophosphoric or sulphuric acid with added hydrogen peroxide were studied. The morphology of the lateral mesa surface degrades as a result of treatment with wet chemical etching solutions, since the rates of etching of heterostructure layers, which have different chemical properties, differ (Fig. 4, *b*). However, the shape distortion is insignificant, overetching along individual heterostructure layers is not observed, and the results of analysis of the effect of surface treatment procedures on the electrical parameters of PVCs revealed a reduction of current leakage seen in dark current–voltage characteristics (Fig. 5). It was found that the removal of the damaged layer in the process of wet etching to a depth of ~ 30 nm with solutions of orthophosphoric or sulphuric acid with added hydrogen peroxide resulted in a slight reduction of current leakage. The best result was obtained in the process of etching to a depth of ~ 100 nm with a solution of sulphuric acid with added hydrogen peroxide: the current leakage was below 10^{-9} A at a voltage lower than 1 V.

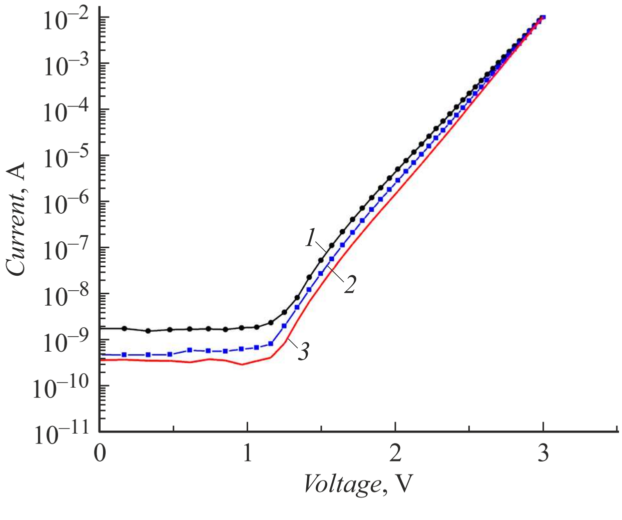

Figure 5. Dark current–voltage characteristics of PVCs after the formation of a dividing mesa-structure by plasmachemical etching: *1* — without treatment, *2* — etching in H_2SO_4:H_2O_2:H_2O for 30 nm, *3* — etching in H_2SO_4:H_2O_2:H_2O for 100 nm.

3. Suppression of PVC degradation upon thermal cycling

Elements with different types of surface treatment were subjected to thermal cycling in order to assess the mesa surface quality and the resistance of fabricated PVCs to degradation. A total of approximately 100 PVCs were examined. Ten cycles involving PVC heating to +85°C, conditioning them at the specified temperature and a humidity of 85% for 20 h, and cooling to −40°C were performed. This type of tests allows one to estimate the resistance of PVCs to high-temperature exposure at high humidity with subsequent cooling to a temperature below the freezing point.

It was found that $\sim 20\%$ of PVCs degrade after thermal cycling if the mesa-structure is formed by plasmachemical etching without any additional surface treatment and removal of the damaged layer. The fraction of degrading PVCs dropped to 10–15% in the case of etching of the damaged layer to a depth of 30 nm in highly diluted etching solutions of orthophosphoric or sulphuric acid with added hydrogen peroxide and decreased further to $\sim 6\%$ when the etching depth was set to 100 nm. The PVC degradation consisted in the emergence of leakage channels in dark current–voltage characteristics: the current leakage increased to more than 10^{-7} A at a voltage below 1 V.

Conclusion

Dark current–voltage characteristics of PVCs were analyzed, and it was found that the state of the lateral surface of the dividing mesa (at the sites of emergence of $p-n$ junctions) after plasmachemical etching and additional surface treatment has a significant influence on the electrical PVC parameters. The presence of a damaged layer with a thickness of just several nanometers (or tens of nanometers) on the lateral mesa surface contributes to parasitic current leakage, since conduction channels form within it. In addition, imperfection of the surface crystalline structure results in a reduction of the PVC resistance to environmental factors (temperature and humidity gradients) and thus accelerates the process of PVC degradation, which consists in the emergence of leakage channels and the corresponding deterioration of photovoltaic characteristics, such as the efficiency and the maximum generated power.

The influence of parameters of plasmachemical etching on the course of the process was analyzed. Nonlinear dependences of the rate of etching of GaInP/Ga(In)As/Ge heterostructure layers on pressure in the chamber, inductively coupled plasma (ICP) power, and bias (RIE) power are an important aspect. These dependences may be attributed to the physical specifics of the process, such as the balance of rates of supply of reagents to the etching region and removal of reaction products.

The parameters of plasmachemical etching of layers of the three-junction PVC GaInP/Ga(In)As/Ge heterostructure were examined and optimized in the context of formation of the dividing mesa-structure. The methods of removal of the damaged layer on the lateral mesa surface were studied, and the number of degrading PVCs was reduced by a factor of 3 (to 6%) by optimizing the process of plasmachemical etching with subsequent surface treatment by wet chemical etching. The current leakage was reduced to less than 10^{-9} A at a voltage below 1 V. The obtained results demonstrated high stability and reproducibility of parameters of PVCs fabricated with the application of the developed post-growth technology.

Conflict of interest

The authors declare that they have no conflict of interest.

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