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S.A. Blokhin ¹ ✉, R.V. Levin ¹, V.S. Epoletov ¹, A.G. Kuzmenkov ¹,
A.A. Blokhin ¹, M.A. Bobrov ¹, Y.N. Kovach ¹, N.A. Maleev ¹,
N.D. Prasolov ¹, M.M. Kulagina ¹, Yu.A. Guseva ¹, Yu.M. Zadiranov ¹,
E.V. Nikitina ², V.V. Andryushkin ³, A.P. Vasil'ev ⁴,
K.O. Voropaev ⁵, V.M. Ustinov ⁴

¹ Ioffe Institute, Saint Petersburg, Russia

² Alferov University, Saint Petersburg, Russia

³ Connector Optics LLC, Saint Petersburg, Russia

⁴ Submicron Heterostructures for Microelectronics Research and Engineering Center, Russian Academy of Sciences (RAS), Saint Petersburg, Russia

⁵ JSC OKB-Planeta, Veliky Novgorod, Russia

✉ blokh@mail.ioffe.ru

Abstract. The influence of technological parameters during the local Zn diffusion from the metalorganic source DEZn in the MOCVD reactor on the surface morphology of the InGaAs and InP layers was investigated. For a long-term process (more than 120 minutes) of local Zn diffusion into InP through the InGaAs surface layer, erosion of InGaAs surface was observed regardless of the material of the dielectric mask (SiO_2 , SiN_x), the method of deposition of the dielectric mask (plasma chemical deposition or chemical vapor deposition) and method of etching of the dielectric mask (plasma chemical etching or liquid chemical etching). The effect of lateral Zn diffusion under the dielectric mask was formed on InGaAs/InP heterostructures has been studied. It was found that the depth of Zn diffusion in lateral direction into InGaAs is several times less than the depth of lateral Zn diffusion into InP layer. At the same time, a decrease in the thickness of the InGaAs surface layer leads to an increase in the depth of lateral diffusion of Zn under the mask due to the mechanism of vertical Zn diffusion from the InP:Zn region into the InGaAs surface layer.

Keywords: zinc diffusion; surface morphology; diethylzinc; indium phosphide; indium gallium arsenide

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Introduction

The Zinc (Zn) diffusion into AIII B^V compounds makes it possible to form local regions with a required depth and a controlled profile of electrically active p-type dopant. That process is widely used for the fabrication of various optoelectronic and photonic devices [1–2] including avalanche photodiodes (APDs) based on InP/InGaAs heterostructures with separate photon absorption regions in InGaAs layer and multiplication of photogenerated charge carriers in the InP layer [3–4]. There are several main approaches to the diffusion process: diffusion in a sealed ampoule [5–6], Zn diffusion from the applied coating [7–8], Zn diffusion through a narrow gap using a planar source [9–10], diffusion from the vapor phase in an open tube [11–12]. Zn diffusion from the vapor phase in an open tube is the most preferable since it simultaneously ensures high uniformity of Zn diffusion over the sample area and reproducibility of the process.

Traditionally, a dielectric mask based on SiN_x is used to carry out the local diffusion process [13–14] because it allows to make diffusion process at elevated temperatures [15–18]. A dielectric mask based on SiO₂ also provides the required impermeability of Zn at moderate temperatures [19–20] and can be used to create an APD based on the A^{III}B^V material system [8,10,21–23]. The choice of dielectric is due not only to the availability of the appropriate dielectric deposition technology but also be related to the features of the dielectric mask formation technology. Thus, several studies have noted the problem of a sharp increase in APD dark counts when using plasma chemical etching to form a surface relief in InP within the photosensitive region necessary to obtain a two-stage front of the distribution of a p-type dopant in a single Zn diffusion process [24]. In fact, the effect of trap-assisted tunneling [25] can be enhanced in comparison with liquid chemical etching of InP [26] apparently caused by defects introduced into InP during the plasma chemical etching process. It can be assumed that the transition from plasma chemical etching to liquid chemical etching during the formation of a dielectric mask may affect the characteristics of the APD.

In this paper we present the results of a study of the local Zn diffusion from the diethylzinc (DEZn) metalorganic source process technological parameters on the surface morphology of InGaAs and InP layers effect and considers the effect of lateral Zn diffusion into InGaAs/InP under a dielectric mask depending on the thickness of the InGaAs surface layer.

Experiment

The InGaAs/InP heterostructures were grown on InP substrates and consisted of undoped InP 3.5 μm thick layer, an undoped InGaAs 50 nm thick layer, an undoped InAlAs 10 nm thick stop-layer and an undoped InGaAs 250 nm thick surface layer (type I heterostructures). Type II heterostructures were formed from type I heterostructures by sequential selective chemical etching of the InGaAs surface layer and the InAlAs stop-layer. Type III heterostructures were formed from type II heterostructures by selective chemical etching of the InGaAs layer down to undoped InP layer.

The process of Zn diffusion from the vapor phase into InGaAs/InP heterostructures was produced at the MOCVD Aixtron AIX-200 system and DEZn was used as a metalorganic source of Zn with the flow of DEZn $\sim 2.5 \cdot 10^{-5}$ mol/min (a thermostat temperature was 17 °C). The Zn diffusion process was performed at a temperature of 500 °C and a reactor pressure of 50–200 mbar. To prevent deterioration of the InGaAs and InP surface morphology at temperatures above 400 °C a stabilizing flows of AsH₃ and PH₃ was fed into the reactor respectively.

To carry out local Zn diffusion process a dielectric mask was formed on the surface of the studied InGaAs/InP heterostructures using either SiN_x obtained by plasma chemical deposition, or SiO₂ obtained by plasma chemical deposition or by chemical vapor deposition. The required topology of the dielectric mask was formed using contact photolithography followed by plasma chemical etching or liquid chemical etching of the dielectric. To obtain a

two-stage front of a p-type dopant via a single Zn diffusion process a recess with a required shape and etching depth was formed within the dielectric mask window defining the photosensitive area of the APD. The recess was made either by selective chemical etching of the InGaAs layer to the InAlAs stop layer followed by selective removal of the InAlAs stop layer (type I heterostructures) or by chemical etching of InP (type III heterostructures).

After diffusion the studied samples were subjected to ex-situ rapid thermal annealing (RTA) in a nitrogen flow at a temperature of 450 °C for 5 minutes for thermal activation of dopants. To obtain quantitative information about the one-dimensional distribution of electrically active p-type dopants in the InGaAs/InP heterostructure samples after Zn diffusion process electrochemical volt-capacitive profiling (ECV) on the Nanometrics ECVPro electrochemical profiler system was used. The study of the surface morphology of the heterostructures subjected to the local Zn diffusion process was carried out using atomic force microscopy (AFM) on a Veeco Dimension 3100 microscope. Scanning was performed in semi-contact scanning mode (when a probe with a certain resonant frequency touches the sample surface) at room temperature and atmospheric humidity of about 20 % using RTESP probes with a radius of 10 nm. Mathematical analysis of the obtained images allows us to determine several metric parameters of the surface topology. The R_{\max} parameter represents information about the maximum height difference of the profile within the base (studied) length, while the R_z parameter gives information about the average absolute value of the five highest peaks and five deepest pits within the base length. However, to statistically describe the measured surface roughness the standard deviation of the heights of surface irregularities over the sample area R_q is more useful.

To obtain information about the two-dimensional distribution of electrically active p-type dopants in the studied samples the scanning electron microscopy (SEM) method was used. The position of the diffusion front of the Zn dopant was determined by the contrast boundary in the cross-sectional images of the samples between regions with different types of dopants. SEM images were obtained in the secondary electron mode at low (<5 keV) accelerating voltages.

Results and discussion

Our earlier studies of the Zn diffusion process from the vapor phase into InP through the InGaAs surface layer (type II heterostructures) showed that the minimum temperature of the Zn diffusion process is limited by the precipitation of Zn compounds in the solid phase below 460 °C and by the deterioration of the morphology of the InGaAs surface above 550 °C [27]. At the same time to achieve a necessary Zn diffusion depth (more than 2-2.5 μm with a thickness of undoped InP of about 3-3.5 μm) it is necessary to either extend the process time or increase the reactor pressure (see Fig. 1). However, temperature and pressure have a complex effect on the amount of p-type dopant introduced into InGaAs/InP layers. Thus, an increase in the reactor pressure leads to an increase in the maximum concentration of electrically active p-type dopants in the InP layer, while an increase in the temperature leads to a decrease in the concentration of holes.

Studies of the type I-II heterostructures surface morphology after local Zn diffusion process into InP layer through the InGaAs surface layer using a SiN_x dielectric mask have shown that for short duration (60 minutes) of the Zn diffusion processes the surface roughness of InGaAs:Zn does not exceed $R_q \sim 0.2\text{-}0.3$ nm within a scanning area of 5×5 μm , which is at the level of atomic steps of a semiconductor substrate. However, in this case, in order to ensure the required depth of the p-type dopant it is necessary to increase the reactor pressure, which is accompanied by precipitation of Zn compounds in the solid phase [28], the intense defect formation, and the appearance of deep centers in the InGaAs:Zn/InP:Zn diffusion region due to the high concentration of Zn atoms [29–30].

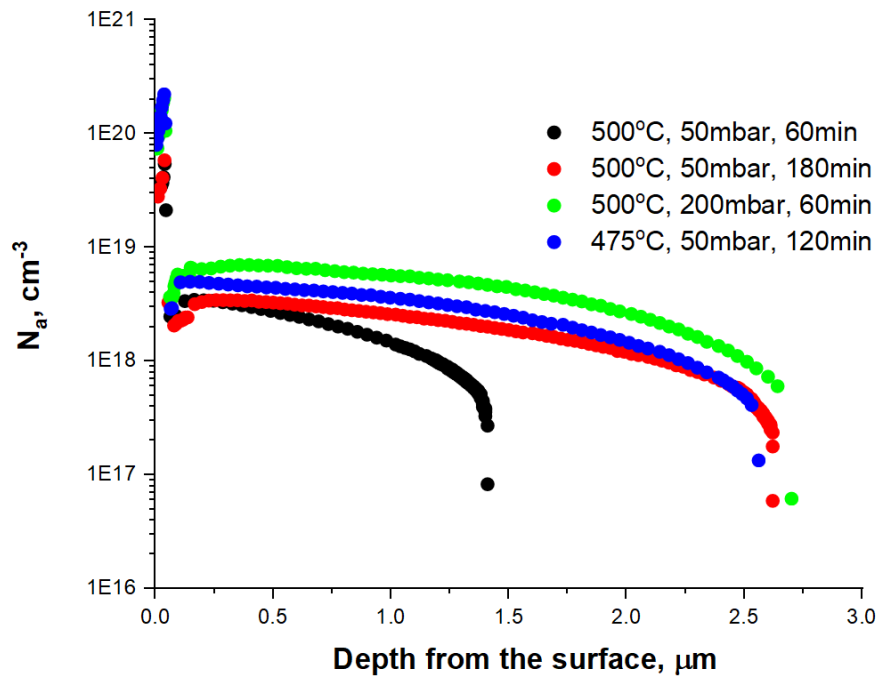


Fig. 1. ECV distribution profiles of electrically active p-type dopant in a type II heterostructure for various technological parameters of Zn diffusion into the InP layer through InGaAs

An increase in the duration of the Zn diffusion process to 180 minutes leads to erosion of the InGaAs:Zn surface (see Fig. 2). AFM measurements indicate a sharp increase in the roughness of the InGaAs:Zn surface to $R_q \sim 2.4$ nm within a scanning area of 5×5 μm . A further increase in the time only aggravates the erosion of the InGaAs:Zn surface. It should be noted that an increase in the stabilizing flow of group V elements not only does not suppress this negative effect, but also increases the probability of precipitation of Zn compounds in the solid phase. On the one hand, deterioration of the InGaAs:Zn surface morphology (type I and II heterostructures) is not observed in the case of Zn diffusion into InP through the InGaAs layer without using a SiN_x dielectric mask, even for long-term Zn diffusion processes. On the other hand, the attempts made to additionally treat the InGaAs surface within the windows of the dielectric mask, including selective liquid chemical etching of the InGaAs surface layer, does not give a solution of the problem of InGaAs:Zn surface erosion during the local Zn diffusion process. It is possible that the observed degradation of the InGaAs:Zn surface morphology is associated with the modification of the InGaAs surface during plasma chemical deposition and/or plasma chemical etching of the SiN_x dielectric.

To exclude the possible negative effect of plasma chemical etching of the SiN_x dielectric on the InGaAs surface layer, it was proposed to switch to a SiO_2 dielectric mask, for which liquid chemical etching of the dielectric can be used when forming the required topology of the dielectric mask. In addition, it was decided to test two types of SiO_2 dielectric formed by plasma chemical deposition and by chemical vapor deposition. However, AFM studies of heterostructures with the SiO_2 dielectric mask after the local Zn diffusion process into InP through the InGaAs layer showed the retention of the problem of InGaAs:Zn surface erosion during long-term diffusion processes regardless of the type of etching of the dielectric and method of mask formation.

Similar studies of local Zn diffusion process directly into InP (type III heterostructures) have been carried out. It should be noted that the Zn diffusion process into InP layer from the vapor phase using a DEZn source is less studied, apparently due to a lower maximum concentration of a p-type dopant [11,31–32] compared with the case of using dimethylzinc

(DMZn) as a metalloorganic source of Zn [11,33–34]. According to our research, there is a similar behavior of the p-type dopant depth from the process time, temperature, and reactor pressure. However, the maximum concentration of electrically active p-type dopant in the InP layer is 2-3 times lower than the Zn diffusion into InP through the InGaAs layer (see Fig. 3). It can be assumed that the observed difference in the concentration of electrically active p-type dopant is related to the charge of elements diffusing through the interstitial-substitutional mechanism [35–36].

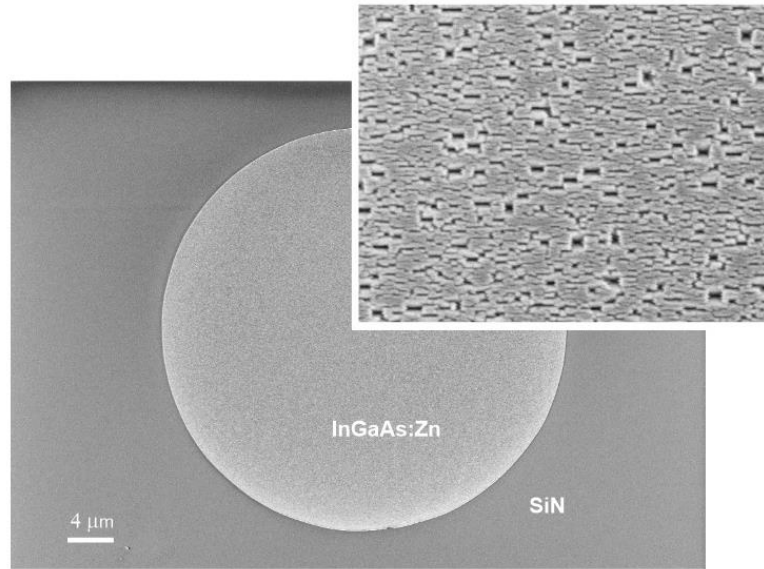


Fig. 2. SEM image (top view) of a sample with local Zn diffusion in InGaAs/InP through a SiN_x dielectric mask (type I heterostructure). The inset shows a SEM image of the sample within the central window. Temperature 500 °C, pressure 50 mbar, process time 180 min

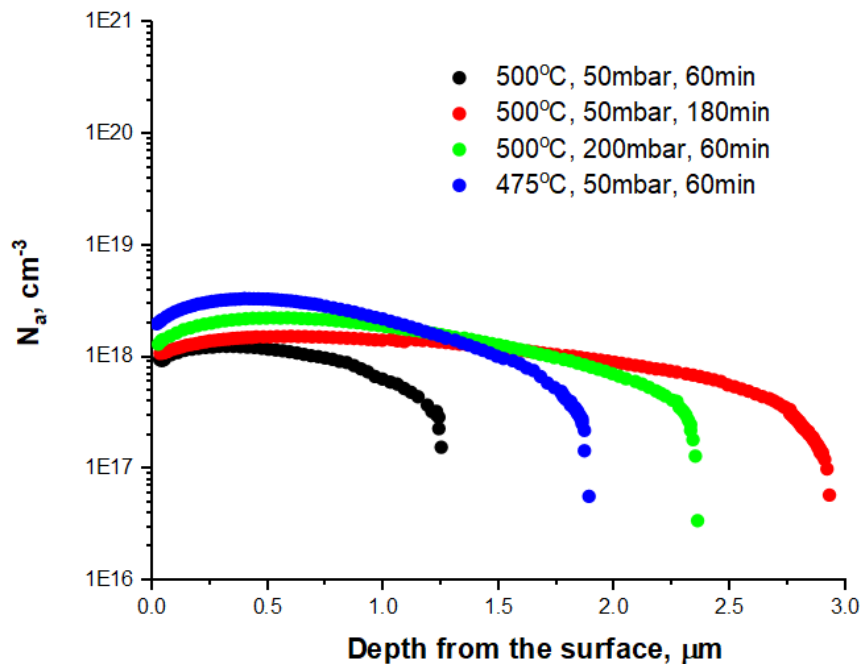


Fig. 3. ECV distribution profiles of electrically active p-type dopant in a type III heterostructure for various technological parameters of Zn diffusion into the InP layer

Studies of the type III heterostructures surface morphology after local Zn diffusion into InP layer during the supply of a stabilizing PH₃ flow did not reveal signs of erosion of the InP surface regardless of the type of dielectric mask and the method of its formation as well as the process time and reactor pressure (see Fig.4). Surface roughness InP:Zn does not exceed $R_q \sim 0.2\text{-}0.3$ nm within a scanning area of 5×5 μm . Moreover, there is no precipitation of any Zn compounds in the solid phase unlike the Zn diffusion into InP through InGaAs under identical technological conditions.

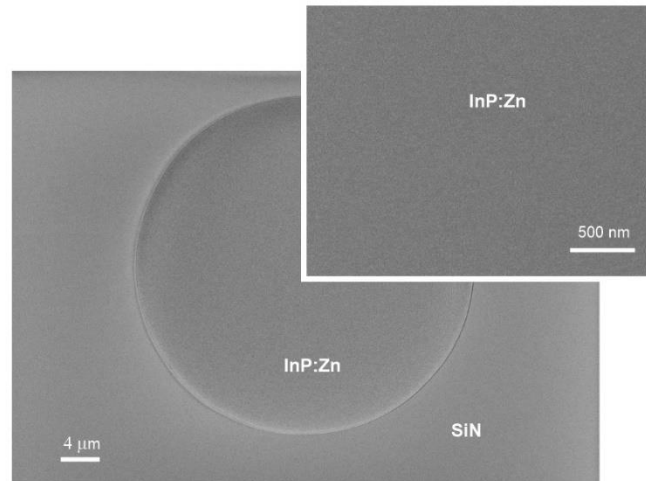


Fig. 4. SEM image (top view) of the sample with local Zn diffusion into the InP through a SiN_x dielectric mask (type III heterostructure). The inset shows a SEM image of the sample within the central window. Temperature 500 °C, pressure 50 mbar, process time 180 min

Thus, on the one hand, the local Zn diffusion into InP layer through InGaAs allows for a high level of doping in the InGaAs surface layer, but it is associated with the problem of erosion of the InGaAs surface during prolonged processes, as well as with the precipitation of Zn compounds in the solid phase at elevated pressures and/or an increase in the stabilizing flow of group V elements. On the other hand, the local Zn diffusion into InP provides a high quality of the InP:Zn surface morphology but is associated with the problem of forming an ohmic contact to the InP:Zn layer. At the same time, to simplify the manufacture of APDs, it is preferable to use InGaAs contact layers to form high-quality ohmic contacts.

One of the possible solutions is to use the effect of Zn diffusion in the direction along the layers of the heterostructure under the dielectric mask [14]. According to our studies of the local Zn diffusion into the InP layer through the InGaAs layer, the lateral Zn diffusion under the dielectric mask depends on the surface concentration of the diffusant: with increasing concentration, the depth of lateral Zn diffusion increases. In the case of a thick surface InGaAs layer (type I heterostructure) the lateral Zn diffusion into the InP layer under the mask reaches 1-1.5 μm (see Fig. 5) for technological modes providing a required depth of Zn diffusion (see Fig. 1). At the same time, the lateral Zn diffusion into the InGaAs layer under the mask varies in the range of 0.4-1.5 μm depending on the thickness of the InGaAs surface layer. Moreover, the morphology of the InGaAs:Zn surface does not deteriorate, because it is protected by a dielectric mask. A decrease in the thickness of the InGaAs surface layer leads to an increase in the effect of lateral Zn diffusion under the mask in the underlying InGaAs/InP layers. The lateral Zn diffusion depth into the InP layer exceeds 2.5 μm for the extreme case (type III heterostructure). Thus, locally preserving a thin near-surface InGaAs layer (20-50 nm) under the protection of a dielectric mask, it is possible to simultaneously provide the p-type doping of this layer due to lateral Zn diffusion from the InP:Zn layer into the InGaAs layer and prevent erosion of the InGaAs:Zn surface (see Fig. 6).

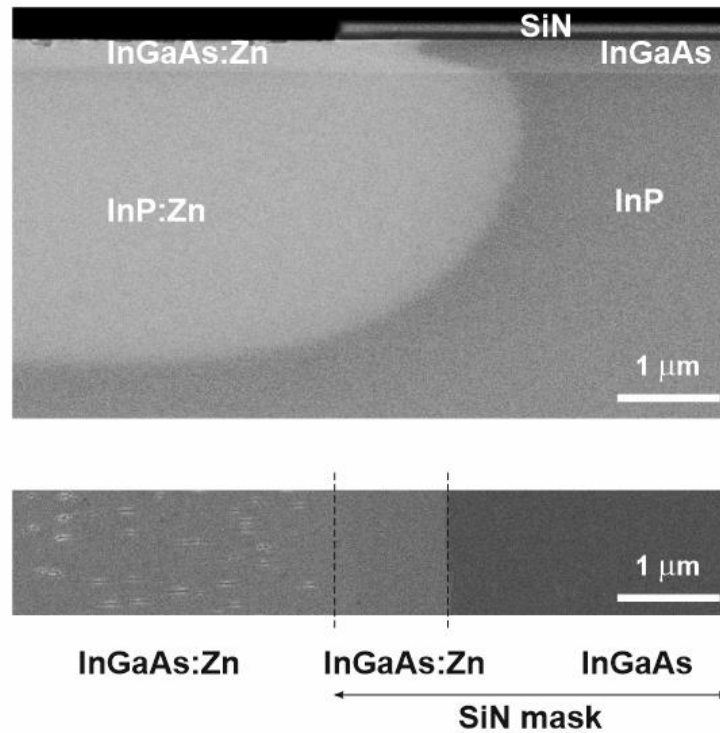


Fig. 5. SEM image of a cross-section of the sample with local Zn diffusion into InGaAs/InP through a SiN_x dielectric mask (type I heterostructure) at the edge of the dielectric mask. The inset shows a SEM image (top view) of the sample on the edge of the dielectric mask after removing the dielectric mask. Temperature 500 °C, pressure 50 mbar, process time 180 min

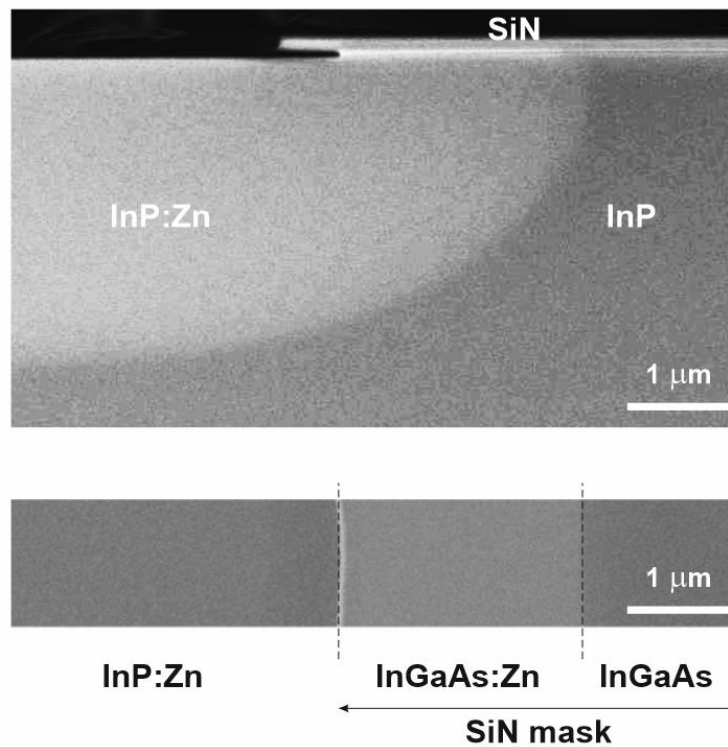


Fig. 6. SEM image of a cross-section of the sample with local Zn diffusion into InGaAs/InP through a SiN_x dielectric mask (type II heterostructure) at the edge of the dielectric mask. The inset shows a SEM image (top view) of the sample on the edge of the dielectric mask after removing the dielectric mask. Temperature 500 °C, pressure 50 mbar, process time 180 min

Conclusion

The analysis of local Zn diffusion from the DEZn metalorganic source technological parameters on the morphology of the InGaAs and InP layers surface is presented. It is shown that for long-term processes of Zn diffusion into InP through InGaAs layer erosion of the InGaAs:Zn surface is observed independent of the dielectric mask (SiO_2 , SiN_x) material and the method of its formation (plasma chemical deposition or chemical deposition from the vapor phase, plasma chemical etching or liquid chemical etching) and also an increase in the stabilizing flow of group V elements leads to an increase in the probability of Zn compounds precipitation in the solid phase. For short Zn diffusion processes it is necessary to increase the surface concentration of the diffusant (decrease in temperature and/or increase in pressure in the reactor) which is associated with defect formation and the appearance of deep centers in the diffusion region due to the high Zn atoms concentration. In the case of Zn diffusion directly into InP layer these problems are not observed. However, the maximum concentration of holes in the near-surface region does not exceed $3 \cdot 10^{18} \text{ cm}^{-3}$, which makes it difficult to form ohmic contacts to InP:Zn layer.

The effect of lateral Zn diffusion into InGaAs/InP under a dielectric mask is considered. The influence of the diffusant surface concentration and the thickness of the InGaAs surface layer on the depth of lateral Zn diffusion under the mask was investigated. It was found that the lateral Zn diffusion in InGaAs layer is several times less than the lateral Zn diffusion in InP layer but there is a vertical component of the Zn diffusion from InP:Zn into the InGaAs surface layer. Due to this a decrease in the InGaAs surface layer thickness leads to an increase in the Zn doping depth in the lateral direction.

The studies have shown the fundamental possibility of simultaneously locally forming a necessary p-type dopant distribution profile in InP layer and p-type InGaAs contact layer during a single Zn diffusion process from the vapor phase in the MOCVD reactor without deterioration of the contact surface morphology.

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THE AUTHORS

Blokhin S.A. 
blokh@mail.ioffe.ru


Epoletov V.S. 
vadep@yandex.ru


Blokhin A.A. 
Aleksy.Blokhin@mail.ioffe.ru


Kovach Y.N. 
yakovachyakov@gmail.com

Prasolov N.D. 
Nikpras@mail.ioffe.ru


Guseva Yu.A. 
Guseva.Julia@mail.ioffe.ru

Nikitina E.V. 
nikitina@mail.ru

Vasil'ev A.P. 
Vasiljev@mail.ioffe.ru

Ustinov V.M. 
vmust@beam.ioffe.ru


Levin R.V. 
Lev@vpegroup.ioffe.ru

Kuzmenkov A.G. 
kuzmenkov@mail.ioffe.ru

Bobrov M.A. 
bobrov.mikh@gmail.com

Maleev N.A. 
maleev.beam@mail.ioffe.ru

Kulagina M.M. 
Marina.Kulagina@mail.ioffe.ru

Zadiranov Yu.M. 
Zadiranov@mail.ioffe.ru

Andryushkin V.V. 
vlad.andryushkin@connector-optics.com

Voropaev K.O. 
kirill.voropaev@novsu.ru