Zn diffusion technology for InP-InGaAs avalanche photodiodes

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Abstract. This paper presents a study of Zn diffusion process into InP and InGaAs/InP epitaxial heterostructures grown by molecular beam epitaxy. It was found that both diffusion systems: a resistively heated quartz reactor with a solid-state Zn vapor source placed inside and hydrogen or nitrogen as the carrier gas and MOCVD reactor with hydrogen as the carrier gas allow achieving similar dopant concentration above 2*10e18 cm⁻³. The depth of the diffusion front in the InP layer is located from 2 to 3.5 µm depending on the temperature and time of the diffusion process. The diffusion of Zn into InP through the intermediate InGaAs layer provides better surface quality comparing with direct zinc diffusion into InP surface.

1. Introduction
Zn diffusion process is widely used to fabricate multiplication region of avalanche photodiodes (APD) based on InP-InGaAs heterostructures, including single photon detectors in telecommunication spectral range [1-4]. The concentration profiles of electrically active dopants significantly affect on main characteristics of APD, e.g. edge breakdown voltage. The Zn diffusion rate and diffusion coefficient strongly depend on the temperature and concentration (quadratic dependence on concentration) [5-8]. Thus, precision control of the diffusion depth and the concentration profile of the dopant are the key elements of the technology for the realization of APDs with required parameters. Among the actual problems of the Zn diffusion technology in InP layers are the relatively low values of the limiting concentration of holes which complicates the formation of ohmic contacts and the difficulty of preserving the quality of the InP layer surface during the diffusion process. A possible decision is to implement diffusion through an additional thin InGaAs layer [9, 10], but the features of the diffusion process in such structures were not sufficiently studied.

2. Experiment
To develop the production technology for planar InP-InGaAs APDs, the features of Zn diffusion in the epitaxial structures of InP and InGaAs/InP grown by molecular beam epitaxy (MBE) on semi-insulating InP substrates were studied. The structures contained epitaxial layers of undoped InGaAs with a nominal thickness of 0.3 µm. The composition and thickness of the grown epitaxial layers were controlled by high-resolution X-ray diffraction system. Zn diffusion was carried out using two systems: (1) a resistively heated quartz reactor with a solid-state Zn vapor source placed inside and hydrogen or nitrogen as the carrier gas; (2) a MOCVD reactor with hydrogen as the carrier gas.
Dieethylzinc (DEZn) was used as a Zn source, and an arsine stream was fed into the reactor to prevent degradation of the InGaAs surface. In both cases, the temperature of the diffusion process was 440-500°C. At the first stage, the surface of the samples was not protected by any mask, and after diffusion, all samples were subjected to activation annealing in a quartz reactor in a stream of extremely pure nitrogen at a temperature of 450-455°C. The heating time was 10 minutes, the holding time at a constant temperature was 3 minutes. The concentration profiles of Zn, Ga, As, P, and In atoms after diffusion were studied by secondary ion mass spectrometry (SIMS). The concentration profiles of an electrically active p-type dopant after diffusion and activation annealing were studied by electrochemical capacitance-voltage profiling (ECV). Optical microscopy and scanning electron microscopy (SEM) were used to control the surface quality of the samples after diffusion and annealing. Local diffusion of Zn through a mask formed by plasma-chemical etching in a 0.3-µm-thick SiNx layer deposited by plasma-chemical deposition was carried out using test APD structures with upper contact layer of InGaAs. The obtained 2D-dimensional concentration profile of the dopant was studied using SEM.

3. Results

Figure 1 shows the concentration profiles of P, Zn, Ga, As, and In in the test epitaxial heterostructure, measured by the SIMS after diffusion in System 1. Figure 2 shows the concentration profile of the electrically active p-type dopant in this structure, measured by the ECV method after diffusion and activation annealing.
Figure 2. The concentration profile of the electrically active p-type dopant in the epitaxial structure, measured by ECV after diffusion in System 1 and activation annealing.

Analysis of the results shows that values of the diffusion front depth measured by the two methods are similar and equal to 3.5-3.7 microns. The doping level of Zn and the concentration level of the electrically active dopant in the InGaAs layer are close to (1.5-2)·10^{19} cm^{-3}, which is sufficient for the formation of p-contacts with low resistance.

Concentration profiles of the electrically active p-type dopant in InGaAs/InP test epitaxial heterostructures after Zn diffusion in two types of systems and activation annealing measured by the ECV method are shown in Figure 3.

Figure 3. Concentration profiles of the electrically active p-type dopant in InGaAs/InP heterostructure on depth measured by ECV.

In both cases, a high concentration of electrically active p-type dopant was achieved in the InGaAs layer (> 4·10^{19} cm^{-3}). At the same time, in the case of using the MOCVD technology, a higher level of doping of the InP layer was observed.

During the Zn diffusion in MOCVD chamber, the sample temperature varied in the range of 420-500°C and the temperature of the DEZn source and the flow of arsin (for samples with
an InGaAs layer on top) or phosphine (for samples with an InP layer on top) varied as well. The parameters to prevent the deposition of metallic Zn on the surface and surface damage during phosphorus evaporation were determined. The optimal conditions for MOCVD were \(~440-445^\circ\text{C}\), for a quartz reactor \(\sim 480^\circ\text{C}\), with an InGaAs layer on top.. The effective flows for the two systems are different, so the diffusion front has a depth range that depends on the temperature and time of the process. That is why the process time was varied to achieve the desired depth. For the MOCVD system, 1 hour process time is optimal for depth of 2.3-2.5 microns, for a quartz reactor it is \(\sim 1.5\) hours.

According to the results of experiments, the values of the depth of the diffusion front range from 2.0 to 3.5 microns depending on the temperature and time of the process were achieved. At the same time, the level of doping of the InGaAs and InP layers differs by an order of magnitude, that correlates well with the different limit levels of Zn penetration depth and data on its accumulation at the heterointerface InGaAs / InP [9]. Due to the difference in Zn diffusion rate in the InGaAs and InP layers, Zn is accumulated at heterointerface during diffusion from InGaAs to InP, which is clearly shown in Figure 3. This effect is occured when using both systems.

Comparative studies of the InGaAs/InP APD heterostructures after Zn diffusion through the windows in the SiNx mask were carried out. It was shown that for the System 1, when using N\(_2\) (Figure 4b) as a carrier gas, the surface quality is better than for H\(_2\), (Figure 4a). In the case of H\(_2\) as a carrier gas, a local accumulation of residual products was observed at the edges of the pattern in the masking layer.

![Figure 4](image-url)

**Figure 4.** Optical microscope images of topology fragments on the surface of InGaAs/InP APD test heterostructures after Zn diffusion in System 1 in (a) H\(_2\) and (b) N\(_2\) gas medium.

Studies of SEM images of test InGaAs/InP APD wafer cross section confirmed the formation of a two-dimensional doping profile with a flat front and a depth close to the designed values (Figure 5).

![Figure 5](image-url)

**Figure 5.** SEM image of InGaAs/InP APD test heterostructure crosssection after Zn diffusion in system 1. The black line indicates the boundary of the diffusion front. The diffusion depth is about 2.3 microns (close to the designed value of 2.5 microns).
4. Conclusion
During the preliminary optimization of the Zn diffusion parameters in the InP and InGaAs/InP epitaxial layers, it was found that a high concentration of an electrically active p-type dopant can be achieved in the InGaAs layers (at the level of \((2-4)\times10^{19}\) cm\(^{-3}\) with an increase to the level of \(~1\times10^{20}\) cm\(^{-3}\) at the interface of the InGaAs and InP epitaxial layers). At the same time, the surface of the heterostructure remains in a satisfactory condition. The values of the depth of the diffusion front, were varied controllably in the range from 2.0 to 3.5 microns depending on the samples temperature and time of the process. According to SEM images a flat diffusion front was achieved.

Further research will focus on the construction of a 2D-model of Zn diffusion in InGaAs/InP structures and detailed studies of the formation of a two-dimensional Zn diffusion profile through windows in a dielectric mask.

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