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Zn diffusion from vapor phase into InGaAs/InP heterostructure using diethylzinc as a p-dopant source

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Abstract. The zinc diffusion process into InP through a thin InGaAs layer using diethylzinc (DEZn) as a p-dopant source was investigated. The distribution profiles of electrically active dopant in InGaAs/InP heterostructures were obtained by electrochemical capacitance-voltage profiling technique. The influence of temperature and pressure in the reactor, DEZn flow rate and process time on the concentration of holes and the diffusion depth was investigated. The process of zinc diffusion strongly depends on the zinc concentration at the surface, however, the maximum concentration of holes and the depth of zinc diffusion into the InP layer might be chosen independently in a certain range of values.
Keywords: Zink diffusion, diethylzinc, indium phosphide.

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Introduction

Zinc (Zn) diffusion into $A^{III}B^{V}$ compounds allows the formation of p-type areas with a certain diffusion depth and a controlled profile of electrically active dopant. This type of diffusion is widely used for fabrication of optoelectronic devices [1-3] and elements of photonic integrated circuits [4]. Several approaches of Zn diffusion into InP layers are known. The first approach is Zn diffusion from applied coating [5–7]. The second approach is Zn diffusion in sealed-ampoule [8–10]. The third approach is Zn diffusion from a vapor source in an open pipe [11–13]. A distinctive feature of the third approach is the ability to simultaneously ensure high reproducibility of the process and uniformity of diffusion over the sample area.

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The most promising approach for the implementation of Zn diffusion from the vapor phase is the usage of metal organic chemical vapor deposition (MOCVD) system reactors [14,15]. In this case, diethylzinc (DEZn) or dimetilzinc (DMZn) are used as a source of Zn. The choice of DMZn as a source of Zn allows to obtain high levels of Zn concentration but leads to use another technological system due to the long-term preservation of a high background level of the p-dopant in the reactor. DEZn as the source of p-dopant is more preferable than DMZn because DEZn has less vapor pressure than DMZn and consequently molar flow of DEZn is easier to control. The Zn diffusion process into InP from a DEZn source is used less frequently and is not much studied due to the lower maximum concentration of a p-type dopant [14,16,17] in InP. This makes it difficult to form high-quality ohmic contacts to the InP:Zn layers (the p-type doping level is typically lower than $6 \cdot 10^{18}$ cm^{-3}). The possible solution of this problem is using of an additional InGaAs layer for the formation of ohmic contacts due to a higher solubility limit of Zn in InGaAs layers (the p-type doping level is typically higher than $1 \cdot 10^{19}$ cm^{-3}) compared to InP layers [18]. In several studies the possibility of Zn diffusion into InP from the vapor phase through a thin InGaAs layer has been experimentally demonstrated [3,4,19,20]. However, detailed studies of the effect of technological parameters of the Zn diffusion process on the distribution profile of the p-type dopant in such heterostructures have not been presented.

In this paper we present results of a study of the features of Zn diffusion process into InP layers through a thin InGaAs layer from a DEZn vapor phase source at reduced pressure, including the dependences of the obtained doping profile on the temperature and pressure in the reactor, on the flow rate of DEZn and the time of the diffusion process.

Method

The InGaAs/InP heterostructures consisted of a near-surface layer of undoped InGaAs 50 nm thick and a subsequent layer of undoped InP 3.5 μm thick. The process of Zn diffusion from the vapor phase into InGaAs/InP heterostructures was performed at reduced pressure (the pressure in the reactor is less than atmospheric) at the MOCVD Aixtron AIX-200 system. DEZn was used as a source of Zn and hydrogen (H_2) was used as a carrier gas. A stabilizing flow rate of group V elements arsin (AsH_3) was fed into the reactor to prevent degradation of the InGaAs surface during diffusion. The flow rate of DEZn was regulated by changing the flow rate of hydrogen through the DEZn bubbler at constant temperature of the thermostat, which was 17 °C. In this case, the choice of temperature was determined by the absence of heating of the corresponding gas line. After the Zn diffusion process, the InGaAs/InP heterostructure samples were cooled first to a temperature of 400 °C in the stabilizing flow of AsH_3 and then to 250 °C in the H_2 flow while increasing the pressure in the reactor to atmospheric.

The distribution profiles of electrically active dopants in the studied heterostructures were determined by electrochemical capacity-voltage profiling (ECV) using Nanometrics ECV Pro system. At large depths of electrochemical etching, the curvature of the etching well can lead to a broadening of the measured doping front. InGaAs/InP heterostructure samples were subjected to an ex-situ process of dopant thermal activation in the nitrogen stream at a temperature of 450 °C for 5 minutes using a rapid thermal annealing (RTA) system after completion of the Zn diffusion process. Without RTA process the ECV concentration of holes in the InP layer typically turns out to be lower than the concentration of the dopant Zn in the InP layer determined by the method of dynamic secondary ion mass spectrometry (SIMS) [4,12,14,15,19]. This difference is usually explained either by the formation of Zn-H compounds during diffusion, when hydrogen passivates nodal atoms of the Zn dopant [22,23], or by the self-compensation effect, when interstitial atoms of the Zn dopant (donor) partially compensate nodal atoms of the Zn dopant (acceptor) [14,23]. An increase of holes concentration after RTA is observed.

The surface morphology of InGaAs/InP heterostructures after Zn diffusion was evaluated using scanning electron microscopy and atomic force microscopy.

Results and discussion

Figure 1 shows the distribution profiles of electrically active p-type dopant in the InGaAs/InP heterostructure depending on the DEZn flow rate at a constant process temperature of 475 °C. The pressure in the reactor was 50 mbar, the process time was 180 minutes. With increasing depth from the surface of the structure to the depth corresponding to the position of the InGaAs/InP interface, there is a sharp drop in the hole concentration from (2-10)$\cdot10^{19}$ cm^{-3} to (2-8)$\cdot10^{18}$ cm^{-3} which coincides with the position of the InGaAs-InP interface. It should be noted that there is a segregation of holes in the InGaAs layer near the heterointerface. This effect is due to the difference in the solubility of Zn in InGaAs and InP and correlates with published data of the Zn diffusion from DMZn [4,18]. Then the hole concentration slowly decreases until the second segment of a sharp drop appears (to the level of $1\cdot10^{17}$ cm^{-3}) associated with the Zn diffusion front [24]. The correct assessment of the dopant concentration in a thin InGaAs layer is difficult because of depletion of the surface during ECV profiling, which underestimates the hole concentration near the surface. As well as the process of reverse diffusion near the surface, which reduces the concentration of Zn [2] and enhances the effect of segregation of holes on the heterointerfaces with an increase of the flow rate of DEZn. The maximum concentration and depth of the p-dopant (at the level of $1\cdot10^{17}$ cm^{-3}) in InP increases with raising of the DEZn flow rate, and the saturation effect at maximum flow rates is observed. Thus, we can assume that the DEZn flow rate~$2.55\cdot10^{-5}$ mol/min makes it possible to obtain close to the limit levels of Zn dopant concentration in the InP layer for this doping method and a constant thermostat temperature of the DEZn source. It should be noted that upon diffusion of Zn from DEZn directly into the InP layer from DEZn the hole concentration typically does not exceed $2\cdot10^{18}$ cm^{-3} [17,16,14] due to the relatively low partial pressure of DEZn [25]. However, the maximum hole concentration can reach the level of $6\cdot10^{18}$ cm^{-3} when Zn diffuses into InP layer from the vapor phase through a thin InGaAs layer which correlates with the Zn diffusion from DEZn through a thick InGaAs layer [19] and is comparable with the results of Zn diffusion from DMZn into InP layer [24,26].

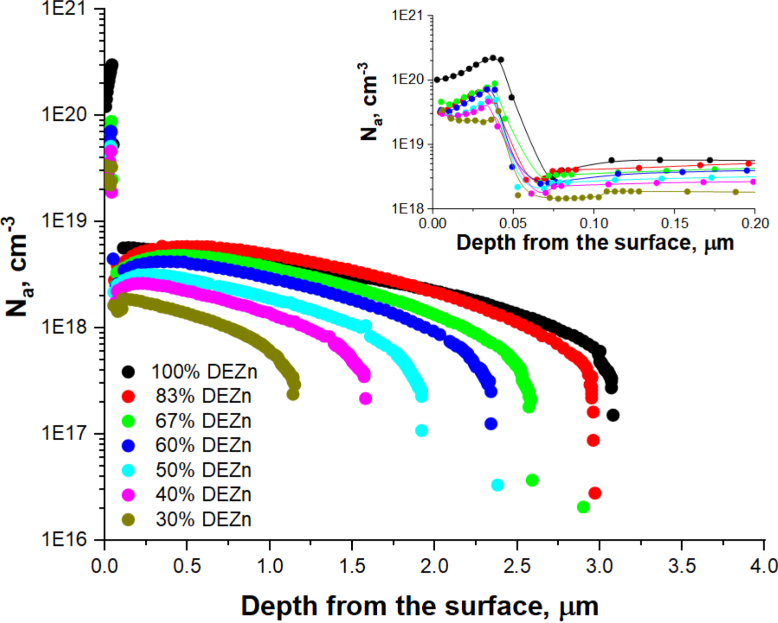

Fig. 1. Distribution profiles of electrically active p-dopants in the InGaAs/InP heterostructure for different levels of DEZn flow rate measured by ECV profiling. Temperature: 475°C, pressure: 50 mbar, process time: 180 min

The results of the influence of temperature in the reactor on the Zn diffusion process with other constant technological parameters are shown in Fig. 2. The distribution profiles of electrically active p-dopants in the InGaAs/InP heterostructure depending on the temperature in the reactor at a maximum DEZn flow rate ($2.55\cdot10^{-5}$ mol/min) and a constant pressure in the reactor (50 mbar) are shown. Diffusion processes were carried out at temperature range from 450 to 550 °C for 180 minutes. At temperatures below 460 °C, precipitation of Zn compounds in the solid phase, for example Zn_3As_2, is observed on the surface of the sample. At temperatures above 550 °C, the morphology of the InGaAs surface deteriorates due to an insufficient level of the stabilizing flow rates of V-group elements [18]. As the diffusion temperature increases, there is a slight decrease in the maximum of hole concentration in the InGaAs layer to $1.5\cdot10^{19}$ cm^{-3}, while the hole concentration and the depth of Zn diffusion into the InP layer changes significantly. Thus, the maximum hole concentration in the InP layer with increasing temperature in the reactor decreases by 5 times from $5.4\cdot10^{18}$ cm^{-3} at 475 °C to $1.1\cdot10^{18}$ cm^{-3} at 550 °C. The diffusion depth is reduced by 3 times from 3.1 μm at 475 °C to 1.1 μm at 550 °C. With an increase of the temperature in the reactor, the effect of holes segregation on the heterointerface is observed. In contrast to the case of diffusion from DMZn [2,18] the complete decomposition of DEZn on the sample surface occurs already at temperatures above 410 °C [27]. Therefore, observed behavior is due to the Zn desorption at high temperatures leading to decrease in the amount of Zn atoms taking part in diffusion process. Thus, temperature range of 475–500 °C should be used for Zn diffusion processes into InP layer to a relatively deep depth of more than 2.5 μm.

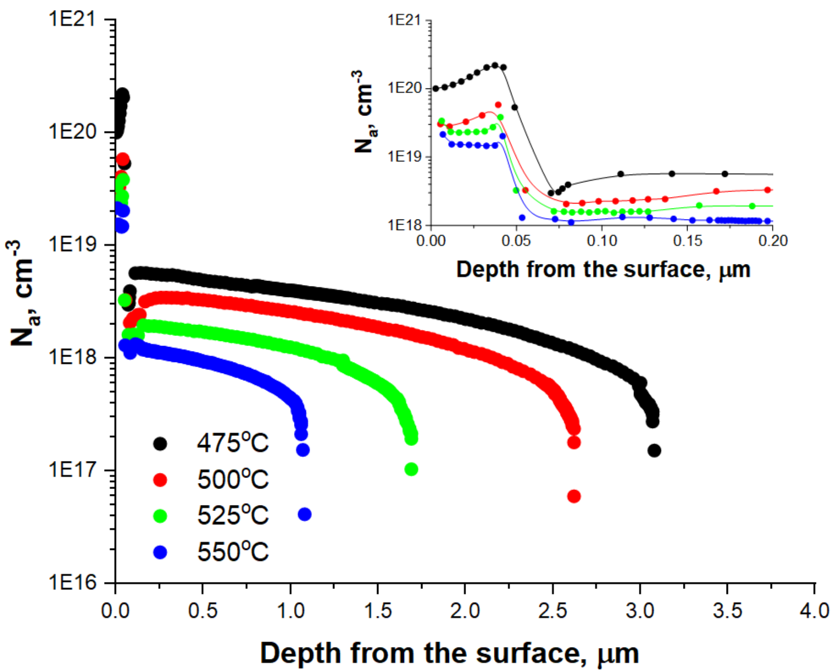

Fig. 2. Distribution profiles of electrically active p-dopants in the InGaAs/InP heterostructure for different Zn diffusion temperatures. Pressure: 50 mbar, max DEZn flow rate, process time: 180 min

The influence of the Zn diffusion process time with other constant technological parameters was also investigated. The experiments were carried out at the maximum DEZn flow rate ($2.55\cdot10^{-5}$ mol/min), constant pressure (50 mbar) and temperature (475 °C) in the reactor. According to Fig.3 the depth of the Zn diffusion front in InP layer demonstrates a root dependence on the process time which correlates with experimental data of the Zn diffusion

from DMZn to InP [15,24] and InGaAs layers [18], as well as the diffusion of Zn from DEZn to InP layer [14,16]. There is an initial transition process where the InGaAs layer is saturated with a p-dopant. There is no Zn diffusion in InP layer until saturation is reached. The maximum hole concentration in the InP and InGaAs layers, as well as the shape of the distribution profiles of electrically active p-dopants in the InGaAs/InP heterostructure does not depend on the diffusion time, except for the initial stage when Zn diffusion occurs only in the InGaAs layer.

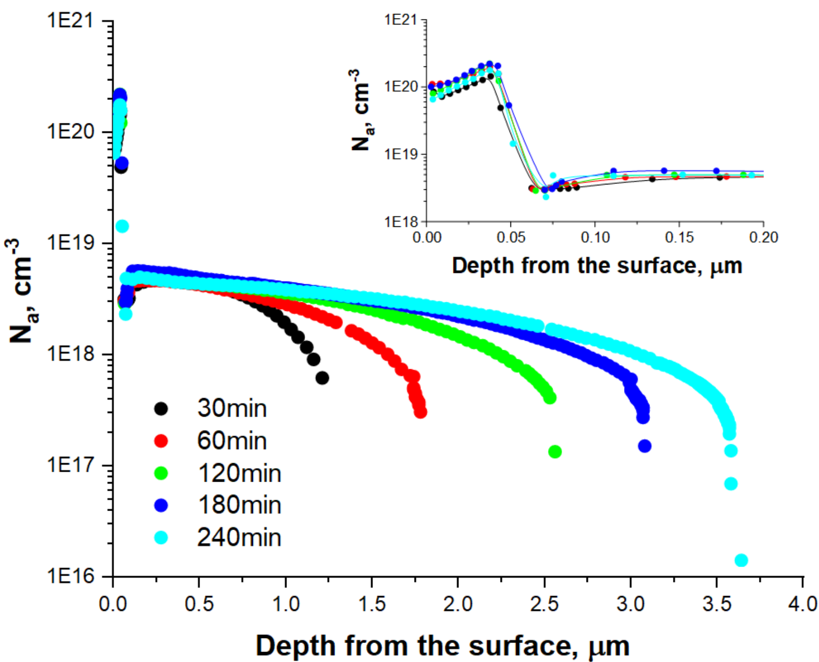

Fig. 3. Distribution profiles of electrically active p-dopants in the InGaAs/InP heterostructure for different Zn diffusion process times. Pressure: 50 mbar, max DEZn flow rate, temperature: 475 °C

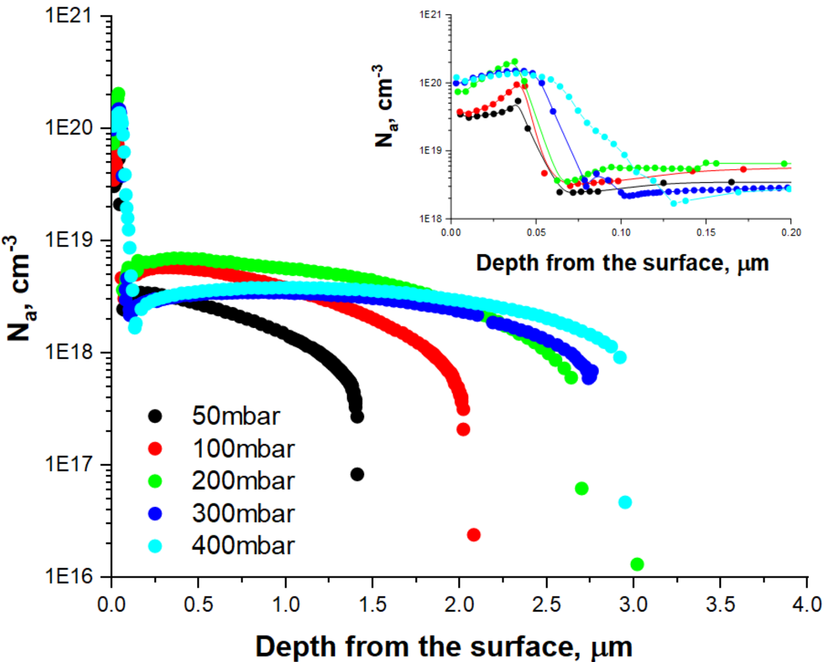

Fig. 4. Distribution profiles of electrically active p-dopants in the InGaAs/InP heterostructure for different pressures. Temperature: 500°C, max DEZn flow rate, process time: 60 min

Figure 4 shows the distribution profiles of electrically active p-dopants in the InGaAs/InP heterostructure depending on the pressure in the reactor at 500 °C, the DEZn flow rate of $2.55 \cdot 10^{-5}$ mol/min and the process time of 60 min. It follows from the presented data that increasing the pressure in the reactor to 200 mbar leads to a sharp increase in the maximum hole concentration in the InP layer from $3.4 \cdot 10^{18}$ cm^{-3} to $7 \cdot 10^{18}$ cm^{-3} and the Zn diffusion depth from 1.4 μm to 2.7 μm. However, at a pressure above 300 mbar a reverse drop in the maximum hole concentration in InP to $3.5 \cdot 10^{18}$ cm^{-3} without a significant change in the Zn diffusion depth is observed. A further increase of pressure does not lead to a noticeable change in the distribution profile of electrically active p-dopants and is associated with a deterioration of the surface morphology (formation of inhomogeneous films). This effect can be caused by a deterioration in the permeability of the InGaAs:Zn layer when the solubility limit of the Zn dopants in InGaAs is reached and by changing the mechanism of Zn diffusion in InP at elevated pressure [15,24].

Conclusion

The results of Zn diffusion into InGaAs/InP heterostructures using diethylzinc as a vapor phase p-dopant source are presented. Analysis of the distribution profiles of electrically active p-dopants in InGaAs/InP heterostructures measured by ECV profiling revealed a significant influence of the DEZn flow rate and pressure in the reactor on the shape of the diffusion profile. Thus, an increase in the DEZn flow rate to $2.55 \cdot 10^{-5}$ mol/min leads to an increase in the maximum concentration and depth of the p-dopant in the InP layer and an increase of the pressure in the reactor to 200 mbar leads to a sharp increase of the hole concentration and diffusion depth. However, at higher pressures, a drop of the maximum hole concentration is observed with a slight increase in the Zn diffusion depth which is due to a deterioration of the permeability of the InGaAs:Zn layer when the solubility limit of the Zn dopants in InGaAs is reached and/or by changing the diffusion mechanism of Zn in InP layer at elevated pressure.

The deterioration of the morphology of the InGaAs surface is observed at temperatures above 550 °C. The precipitation of Zn compounds in the solid phase is observed at temperatures below 460 °C. A decrease of the diffusion temperature leads to a sharp increase of the hole concentration and the Zn diffusion depth into the InP layer due to increase in the near-surface concentration of the p-dopant by the diffusant desorption weakening. At the same time, the diffusion depth of Zn in InP shows the expected square root dependence on the process time considering the initial transition time (diffusion into the InGaAs layer) without significant modification of the shape of the diffusion profile.

The studies confirm good prospects for the practical use of the Zn diffusion process into InP layers through a thin surface InGaAs layer using the MOCVD reactor and DEZn as a source of p-dopant. A high doping level at InGaAs surface layers is easily achieved, which is necessary to ensure good p-contact quality.

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