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Analysis of Zn diffusion process from the vapor phase in InGaAs/InP materials

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A physical approach has been developed to simulate the process of zinc diffusion into InGaAs/InP heterostructures from metalorganic diethylzinc source in a metal-organic chemical vapor deposition reactor. The results of numerical calculations based on the proposed model showed compliance with experimental data on the distribution of electrically active dopants in InGaAs/InP heterostructures obtained by capacitance-voltage profiling. Effective diffusion coefficients in InGaAs/InP materials and their dependences on temperature and pressure have been established. The nonlinear coordinate dependences of the segregation coefficient, unique for each technological process, are determined. Comparison with scanning electron microscopy data of a two-dimensional diffusion profile demonstrated the isotropy of diffusion processes for InGaAs/InP.

Keywords: Diffusion, diethylzinc, dopant, segregation, indium phosphide.

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The use of avalanche photodiodes based on InGaAs/InP heterostructures with separate regions of photon absorption in the InGaAs layer and multiplication of photogenerated carriers in the InP layer is a promising approach to the construction of small-size single-photon detectors operating in the telecommunication spectral range [1]. The key aspect of development of avalanche photodiodes with such a design is the formation of a double doping profile with the use of a p-type dopant in the InP layer. Local diffusion of Zn into InP through a dielectric mask [2] is used for this purpose. Several processing methods are feasible here: diffusion in a sealed ampoule [3], diffusion of Zn from an applied coating [4], diffusion of Zn through a narrow gap with the use of a planar source [5], and diffusion from the vapor phase in an open tube [2]. The last method differs from the other mentioned ones in providing reproducibility coupled with high uniformity of diffusion over the wafer area.

The primary approach to Zn diffusion from the vapor phase involves the use of reactors of metal-organic chemical vapor deposition (MOCVD systems) setups [6]. Diethylzinc (DEZn) and dimethylzinc (DMZn) serve as Zn sources. The use of a DMZn source requires a separate processing unit, since a high background level of the diffusing material persists in the reactor for a long time; the use of DEZn is complicated by the low limiting level of p-type InP doping [5,6], which precludes one from forming a high-quality ohmic contact to such a layer. The latter problem may be solved by using an InGaAs/InP structure with an InGaAs surface layer, which offers a several orders of magnitude higher Zn solubility limit than InP [7].

The development of a physical model for approximating the experimentally obtained distributions of dopant Zn is needed for proper modeling of the process of local diffusion through a dielectric mask. The complexity and multifactorial nature of diffusion processes make it extremely difficult to obtain an analytical solution to this problem.

In the present study, experimental profiles of the distribution of electrically active dopants in InGaAs/InP heterostructures subjected to Zn diffusion from the vapor phase at different reactor pressures and temperatures and different diffusion process durations are modeled numerically within the proposed physical model of Zn diffusion.

In inhomogeneous or heterostructural materials, diffusion is accompanied by segregation of dopant atoms or point defects [8]. This is the reason why concentration distributions $N(x, t)$ of zinc were analyzed within the model of diffusion-segregation dopant redistribution in a layered system of a given geometry (in the present case, the InGaAs/InP material system). The general diffusion-segregation equation, which is derived from thermodynamic principles, characterizes the processes of diffusion and segregation at the same fundamental level as Fick's law [9,10]:

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x}\left[D\left(\frac{\partial N}{\partial x} - \frac{N}{m}\frac{\partial m}{\partial x}\right)\right]. \quad (1)$$

Equation (1) is convenient, since it contains just diffusion coefficient D and dimensionless segregation coefficient

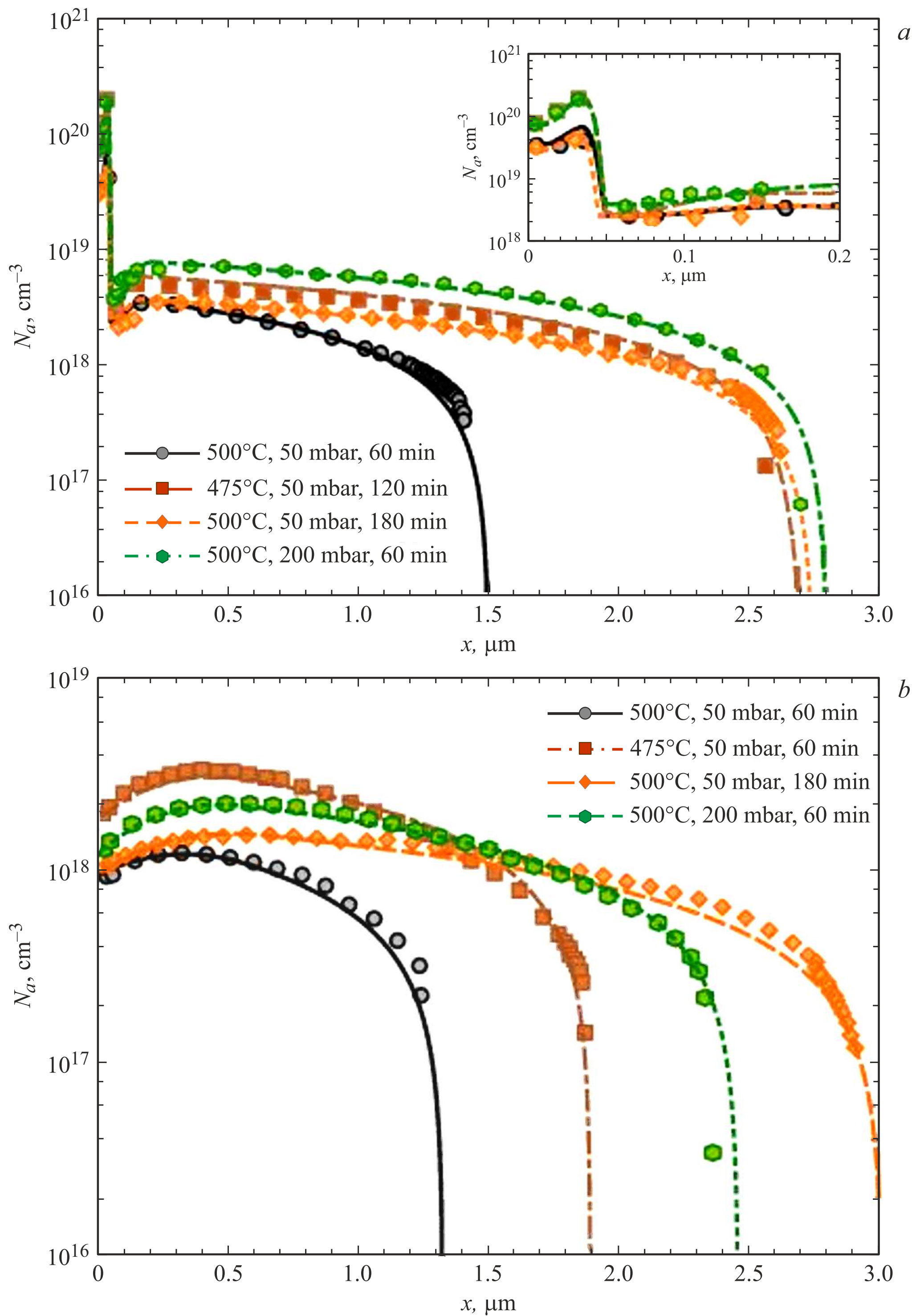

Figure 1. Distribution profiles of electrically active p-type dopants in heterostructures for different process parameters of Zn diffusion measured by ECV profiling. Symbols and curves correspond to the results of experiments and numerical calculations, respectively. a — Heterostructure type A; b — heterostructure type B.

m, which depends on process parameters. In addition, the procedure for calculation of coefficient $m(x)$ may be simplified by normalizing it to segregation coefficient $m(0)$ on the heterostructure surface, which does not entail any transformation of Eq. (1). Parameters D and m are normally treated as experimentally measured thermodynamic quantities, but here they were determined via numerical modeling by finding the best fit to the experimental dopant concentration curves. Equation (1) was solved numerically using the differential mathematics module in Comsol

Multiphysics. Conditions of constancy (Dirichlet condition, $N(0,t) = N_0$) and continuity (Neumann condition) of the dopant concentration were set at the boundaries of the computational domain.

Having analyzed the numerical solution of (1), we found that a simple model of bulk diffusion in a layered system cannot characterize the behavior of the examined heterostructure with sufficient accuracy. The existence of different mechanisms of Zn diffusion (interstitial, vacancy) in InP and InGaAs/InP structures necessitates the introduction of dependence of the diffusion coefficient on the local dopant concentration [11–16]:

$$D(x,t) = D_0\left(\frac{N(x,t)}{N_0}\right)^n, \tag{2}$$

where D_0 is the effective diffusion coefficient and n is an empirical parameter falling within the interval from 1 to 2. This approach is somewhat simplistic, but is used widely in literature and provides a fine description of the available experimental data. In the final numerical model, parameter n was taken equal to 1.

The modeled heterostructures and experimental distributions of electrically active dopants were obtained and characterized in detail in [17]. The initial heterostructures (type A) were grown on an InP substrate and consisted of a layer of undoped InP with a thickness of $3.5\,\mu$m and a layer of undoped InGaAs with a thickness of 50 nm. The studied type B heterostructures were produced by sequential selective chemical etching of the InGaAs layer to undoped InP.

Diffusion of Zn from the vapor phase was carried out in a MOCVD reactor with the use of a DEZn metal-organic source. This diffusion proceeded at a temperature of 475–500°C and a reactor pressure of 50–200 mbar for 60–180 min.

Electrochemical capacitance–voltage (ECV) profiling was performed for the purpose of quantitative assessment of the one-dimensional distribution of electrically active p-type dopants in heterostructures type A and B after Zn diffusion.

The experimental and model data are compared in Figs. 1 and 2. A comparison was made between the one-dimensional distribution profiles of electrically active dopants obtained in modeling and experiments for heterostructures type A and B (Figs. 1, a and b, respectively). It was found that the doping profiles were reproduced accurately in both quantitative (this is evidenced by identical limiting doping levels of layers) and qualitative (with the general nature of coordinate dependence of the distribution and the maximum doping depth taken into account) terms in all technical regimes of Zn diffusion. The available experimental curves may be reproduced with the use of the standard Fick diffusion equation (with segregation neglected). In this case, the analytical dependences are monotonically decreasing functions and deviate from the measurement results in certain regions of the structures under consideration. The deviation is most profound at the surface and at the interface of materials. This inaccuracy in reproducing the experimental data within a simplified model leads to an error in determining the diffusion coefficients, which is especially evident at elevated pressures. It turns out that the segregation coefficient has a significant dependence on coordinate (Fig. 2, a). Zinc segregation in the InGaAs layer near the InGaAs–InP heterointerface is attributable to the difference in limits of Zn solubility in InGaAs and InP. The pressure, temperature, and material type also affect $m(x)$.

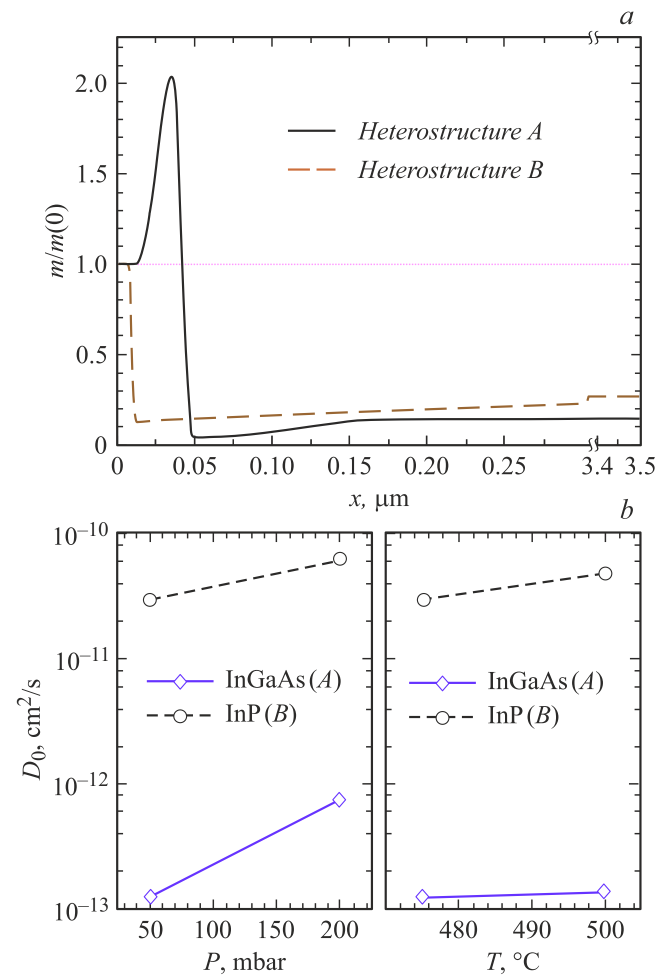

Figure 2. Coordinate dependence of the dimensionless segregation parameter (a) and dependence of the effective diffusion coefficient of layers on temperature and pressure (b) for heterostructures type A and B.

The dependence of effective diffusion coefficients D_0 for each material on temperature and pressure in the reactor was established (Fig. 2, b). Parameter N_0 needed for this was determined from the experimental curves at $x = 0$. An increase in temperature accelerates slightly the diffusion of Zn within the 475–500°C temperature interval. The influence of pressure is more profound. The growth of effective coefficients D_0 with an increase in pressure within the range from 50 to 200 mbar tends to indicate the dominance of interstitial diffusion [18].

Effective diffusion coefficients determined in modeling D_0

Process parameters	D_0, cm^2/s	
	InGaAs	InP
$T = 475^\circ$C, $P = 50$ mbar	$1.33 \cdot 10^{-13}$	$2.99 \cdot 10^{-11}$
$T = 500^\circ$C, $P = 50$ mbar	$1.38 \cdot 10^{-13}$	$4.83 \cdot 10^{-11}$
$T = 500^\circ$C, $P = 200$ mbar	$7.69 \cdot 10^{-13}$	$6.14 \cdot 10^{-11}$

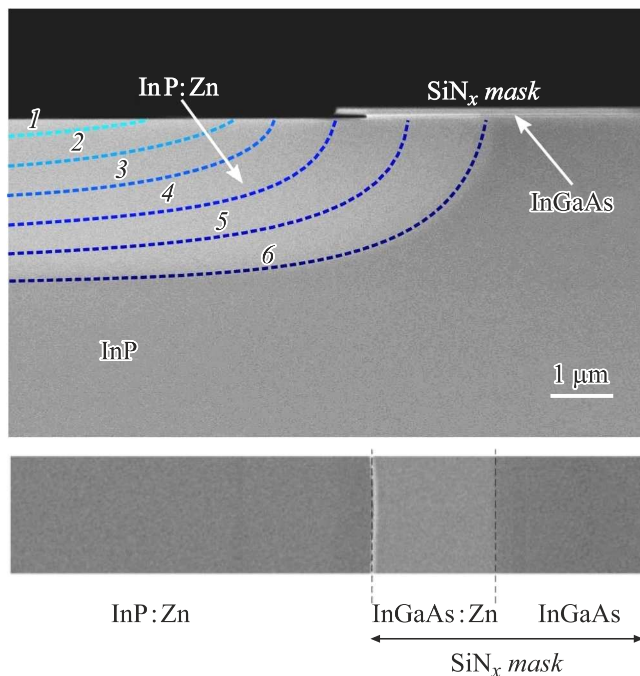

Figure 3. SEM image and results of numerical calculations of the cross section of a sample at the edge of a SiN$_x$ dielectric mask with local diffusion of Zn into InGaAs/InP through this mask. The temperature is 500°C, the pressure is 50 mbar, and the process time is 180 min. Dashed curves *1–6* are the Zn concentration (N_a) profiles obtained by modeling. N_a, 10^{19} cm^{-3}: *1* — 1.30, *2* — 1.07, *3* — 0.83, *4* — 0.59, *5* — 0.35, and *6* — 0.11.

The values of effective diffusion coefficients D_0 determined for each material are listed in the table. These values agree in order of magnitude with the ones reported in literature [13–16].

The growth of effective coefficients D_0 with an increase in pressure within the range from 50 to 200 mbar is indicative of the dominance of interstitial diffusion [18]. The evident agreement between the results of dopant profile modeling and the SEM dopant distribution profile may be indicative of a vertical (surface) nature of segregation variation, since the segregation coefficient distribution established via one-dimensional modeling was used in calculations. It should also be noted that, although the segregation process has a significant influence on the resulting dopant distribution, isotropic effective diffusion coefficient D_0 provides a rather accurate match to the experimental two-dimensional Zn diffusion front. The isotropy of D_0 allows for more accurate estimation of the lateral and vertical diffusion components. Specifically, this provides an opportunity to estimate the required thickness of the InGaAs surface layer protected by a dielectric mask with simultaneous *p*-doping of this layer due to vertical diffusion of Zn into the InGaAs layer from the InP layer doped with Zn owing to lateral diffusion [17].

Thus, it was found that the disregard of segregation processes in modeling of dopant distribution profiles leads to a significant (in certain cases, an order-of-magnitude or greater) error in the determination of effective coefficients D_0. At the same time, the use of a simple model incorporating several (interstitial, vacancy) diffusion mechanisms is sufficient to obtain a fit between the calculated dopant Zn profiles and the measurement data.

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Conflict of interest

The authors declare that they have no conflict of interest.

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