

Experimental studies of the initial diffusion stage in semiconductors

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Abstract

The initial diffusion stage (IDS) of B in Si and Zn in III–V compounds has been studied. The ultra-fast diffusion of Zn in InP has been found at low temperature. An evolution of non-equilibrium defect has been investigated during both IDS and isothermal diffusion. A mechanism of the processes going on IDS has been proposed. © 1998 Elsevier Science B.V.

Keywords: Diffusion; Defects

1. Introduction

The diffusion process has been typically simulated from an analysis of the impurity atom distribution profiles in a semiconductor which were obtained after isothermal diffusion [1–4]. At the same time the initial diffusion stage (an establishment stage at which the temperature of the system rises from room temperature to final temperature T_f corresponding to temperature of isothermal diffusion) has not been considered in most of the theoretical papers. Moreover, experimental results on initial diffusion stage (IDS) are lacking.

A study of the initial diffusion stage (IDS) is of inherent interest for understanding the nature of an atomic interaction in matter, for creating a predictive simulation of the diffusion process and for clarifying

the possibilities of diffusion formation of p – n junctions in semiconductors, among which shallow junctions.

In the present paper we have investigated IDS and the temporal evolution of impurity distribution by comparing the diffusion profiles obtained after isothermal diffusion and after IDS. The temporal evolution of non-equilibrium defects has been judged from the concentration changes of dislocations and microdefects in depth of the diffusion region. The diffusion of boron in Si and zinc in III–V compounds from polymer spin-on films [5,6] has been applied to obtain the experimental results. The possibilities of the diffusion from polymer spin-on films have been investigated in Si, GaAs, InP, and InGaAs. Compared to the conventional diffusion techniques, the diffusion from polymer spin-on films is simpler and more controllable. Moreover, it provides the near-total activation of the impurity atoms introduced by the isothermal diffusion. The peculiarities of the method are associated with a uniform distribu-

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tion of the dopant atoms in the three-dimensional network of the polymer chains. In addition, the maintenance of a V group element vapor pressure is not necessary during the diffusion in III–V compounds because the polymer spin-on film allows a semiconductor surface to be stable against decomposition. These peculiarities make possible the investigation of IDS.

2. Experiment

Diffusion was carried out in (100) Si substrates of *n*- and *p*-types, in undoped *n*-GaAs and *n*-InP ($2 \times 10^{16} \text{ cm}^{-3}$) substrates of (100) orientation, as well as in *n*-InGaAs (10^{15} – 10^{16} cm^{-3}) epitaxial layers. Before diffusion, the wafers were treated using a standard cleaning. Then a polymer film was spun on the wafer surface. Polymer spin-on films doped by B or Zn were used as a diffusion source. The diffusion of B into Si and of Zn into III–V compounds was investigated in the temperature range 800–1000°C and 300–650°C, respectively. Profiles of an impurity atom distribution were investigated by secondary-ion mass spectrometry (SIMS) with an IMS4F (CAMECA) instrument. O_2^+ ions with a net impact energy of 2 keV were used. Quantification of secondary ion count rates data was made using relative sensitivity factors determined from the measurements of ion implanted standards. The crater depth measurements were performed using a DEKTA 3030 surface stylus profilometer. The carrier concentration was determined from *C*–*V* measurements performed with the use of a mercury probe 0.5 mm in diameter. Dislocations and microdefects were revealed by chemical etching. Etch pits appropriated to these defect were denoted *D*-pits and *S*-pits, respectively, according to Ref. [7]. A density of the etch pits was counted with the use of an optical microscope.

3. Results and discussion

The distribution profiles of B and Zn were preliminary investigated for the isothermal diffusion stage. The results were compared with the simulated ones.

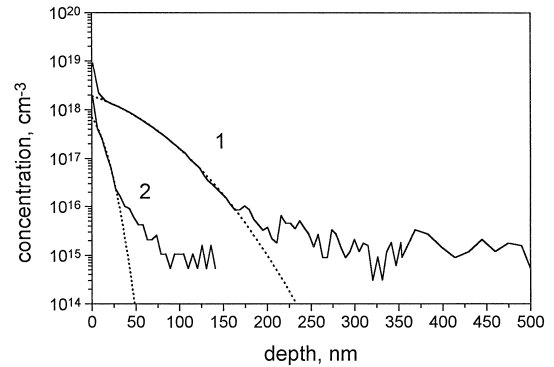


Fig. 1. SIMS distribution profiles of B in Si after: (1) Isothermal diffusion at 900°C for 10 min and (2) IDS at $T_f = 900^\circ\text{C}$. Dotted lines are erfc-function.

Fig. 1 shows the SIMS distribution profiles of boron atoms in Si obtained after isothermal diffusion (curve 1). As may be seen, the profile of the isothermal diffusion is well described by the conventional model (the profile shape is akin to the complementary error function, erfc-function), i.e.:

$$C(x, t) = C_0 \operatorname{erfc} \frac{x}{(Dt)^{1/2}},$$

By contrast, the shape of the Zn profile in the III–V compounds was different which depended on the relation between the Zn concentration in the near-surface region (N_s) of the semiconductor and its solubility limit (L) in the given semiconductor at the diffusion temperature (Fig. 2, curves 1 and 2). The

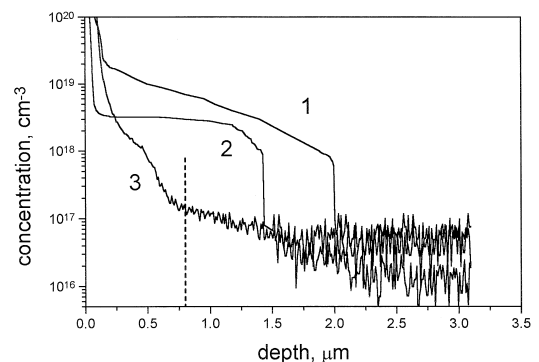


Fig. 2. SIMS distribution profiles of Zn in InP after: (1, 2) Isothermal diffusion at 450°C for 30 min and (3) IDS at $T_f = 375^\circ\text{C}$. (1) $N_s > L$ and (2) $N_s < L$. A dashed line is the *p*–*n*-junction position.

Zn atom SIMS profile obtained at $N_s < L$ was of the typical form, while the anomalous profiles were observed at $N_s > L$. The experimental profiles agreed with the calculated ones which were obtained by the well-known methods based on both vacancy and kick-out mechanisms using appropriate fitting parameters. It should be noted that the shapes of the profiles are similar to the calculated profiles presented in the paper [4,8].

The investigations of IDS showed that the boron distribution profile was not described by the erfc-function (Fig. 1, curve 2). More departures were observed for Zn diffusion in the III–V compounds. That is why an investigation of Zn diffusion in InP has been made in more detail.

It was found experimentally that the Zn diffusion was not detected after IDS at $T_f = 365^\circ\text{C}$. At the same time at $T_f = 375^\circ\text{C}$, the ultra-fast diffusion of Zn was observed. The SIMS profile after IDS at $T_f = 375^\circ\text{C}$ is presented in Fig. 2 (curve 3). The p – n -junction position is also shown here. Rough estimations of effective diffusivity D_{ef} were made. Taking into consideration that Zn diffusion was not found at $T_f = 365^\circ\text{C}$, D_{ef} was no less than $1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ which was at least three orders of magnitude more than D_{ef} obtained after the isothermal diffusion [9–12]. It should be noticed that a ‘diffusion tail’ was always observed on the SIMS profiles obtained after IDS. The ultra-fast diffusion is the characteristic property of IDS. Recently our investigations [13] have shown that the deep penetration of Zn is inherent in IDS, where the penetration depth (d) of Zn has dropped out of the dependence $d^2 = f(t)$ obeyed for the isothermal diffusion (here t is a diffusion time). It should be noticed that an activation energy for IDS differs significantly from that for the isothermal diffusion.

Another characteristic property of IDS is a low activation degree of diffused Zn. An acceptor concentration in the near-surface region was 10^{16} cm^{-3} for IDS at $T_f = 375^\circ\text{C}$. The activation degree increased with increase in T_f , but it did not reach 100%, even at $T_f = 600^\circ\text{C}$. At the same time for the isothermal diffusion for 30 min, the nearly-total activation of diffused Zn was observed at 500°C . An evaluation of T_f caused the progressive transformation of the IDS distribution profile of Zn to the profile approximating the one for the isothermal

diffusion. It should be noticed that a plateau in the Zn atom distribution in semiinsulating InP doped with Fe was formed even after IDS at $T_f > 450^\circ\text{C}$ [13].

As would be expected, an intensive generation of non-equilibrium defects occurred in the diffusion region at IDS (see Table 1). However, simultaneously with the generation, the relaxation of these defects began. As a result, a lot of microdefects and dislocations was formed at IDS. An elevation of T_f caused a decrease in the non-equilibrium defect density which was generated at lower T_f . As the studies showed, IDS significantly determined features of the impurity distribution profiles observed after the isothermal diffusion.

It could be proposed that the peculiarities observed at IDS are association with the competitive vacancy [2] and kick-out [3] mechanisms. The contributions of these mechanisms to the formation of the impurity distribution profiles vary with changes of temperature and of the relation between N_s and L . When temperature is elevated and the vacancy concentration increases, annihilation of self-interstitials and vacancies is capable of playing an important part in the impurity diffusion. The annihilation may cause the abrupt retardation of diffusion front, resulting in an elimination of the ‘diffusion tail’ on the impurity distribution profile.

Table 1

Density of defects revealed at various depth of diffusion layers in undoped InP after IDS ($T_f = 450^\circ\text{C}$ and after isothermal diffusion at 450°C for 30 min)

Diffusion	Depth (μm)	Defect density (cm^{-2})	
		S-pits	D-pits
IDS	0.5–0.8	$> 10^5$	2.4×10^4
	1.5	1.6×10^4	7×10^3
	2–3	6×10^3	6×10^3
	5	6×10^3	6×10^3
Isothermal $N_s > L$	0.5–0.8	$\sim 10^5$	8×10^3
	1.5	4×10^3	5×10^3
	2–3	4×10^3	5×10^3
	5	4×10^3	5×10^3
Isothermal $N_s < L$	0.5–0.8	1.1×10^4	6×10^3
	1.5	7×10^3	4×10^3
	2–3	7×10^3	4×10^3
	5	7×10^3	4×10^3

4. Conclusion

The initial diffusion stage of B in Si and Zn in III–V compounds was studied. The ultra-fast diffusion of Zn in InP was found at low temperature. An evaluation of the diffusion temperature was established to cause a transformation of the impurity and defect distribution profiles. The investigations of IDS and of an evolution of the non-equilibrium intrinsic defects during both IDS and the isothermal diffusion stage are required in more detail in order to develop a simulation.

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