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Zn diffusion enhancement of interdiffusion in a GaInAsP-InP heterostructure

H.-H. Park, B. K. Kang,^{a)} E. S. Nam, and Y. T. Lee

Electronics and Telecommunications Research Institute, Deadog Danji, Deajeon 305-606, Korea

J. H. Kim and O'D. Kwon

Department of Electrical Engineering, Pohang Institute of Science and Technology, Pohang, Kyungbuk 790-330, Korea

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The influence of concurrent Zn diffusion on the interdiffusion in a $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ -InP heterostructure ($x = 0.28, y = 0.61$) was investigated using Auger electron spectroscopy and secondary-ion mass spectrometry. The measured profiles showed that the Zn diffusion (600 °C, 1–4 h) predominantly enhanced the cation (In-Ga) interdiffusion. The result could not be interpreted by the Zn-vacancy complex model. Under conditions of a group V overpressure, our results suggest that cation interstitials may control both the rate of Zn diffusion and the mixing of the group III sublattices in the InP-based alloy system.

Impurity diffusion enhancement of interdiffusion (IDEI) in a III-V heterostructure has been the main theme of several recent papers^{1–8} to study impurity diffusion and self-diffusion. The observations of IDEI have led to an insight into the role of impurity-induced crystal defects on the movement of host atoms, which was overlooked in the existing impurity diffusion models.^{9–11} Several mechanisms for IDEI, in particular for Zn and Si DEI in the GaAs-based alloy systems, have thus been proposed considering electrical interactions between the dopant and the crystal defects^{1–4} and/or modifying a diffusing defect species.^{4,6} In addition, it has been pointed out that an experimental investigation on the differences in diffusion enhancement on cation (group III) and anion (group V) atoms would be informative to test the proposed mechanisms and to clarify the dominant defect governing the impurity diffusion.^{2–4} In recent reports on Zn diffusion in InAlGaP-GaAs⁵ and InGaPAs-GaAs⁷ heterostructures, it has been demonstrated that IDEI due to Zn diffusion occurs predominantly on group III atoms. These results strongly support the proposal⁴ that the group III interstitial is the dominant defect responsible for the alloy mixing and the Zn diffusion.^{5,7}

In contrast to the Zn diffusion in GaAs, a dominant defect related to Zn diffusion in InP is widely known to be a complex of a Zn atom and two P vacancies ($V_p\text{Zn}V_p$).^{12,13} However, the IDEI behavior in InP-based alloy systems is not well established, and the validity of the complex model has not been examined through the observation of IDEI. In the present work, we report that the predominant intermixing of group III atoms due to Zn diffusion is also observed in a $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ -InP ($x = 0.28, y = 0.61$; emitting at a wavelength of 1.3 μm) heterostructure. Our results are not consistent with the expectation from the complex model, but rather consistent with a mechanism involving a group III interstitial, similar to that in the GaAs-based structures.

For this study, undoped GaInAsP layers (0.8–2 μm thickness) were grown on (100) S doped ($6 \times 10^{18} \text{ cm}^{-3}$) InP substrates by a conventional liquid phase epitaxy (LPE)

growth technique using a horizontal furnace under hydrogen gas ambient. In order to reduce the influence of pre-doped S in the substrate on alloy mixing, a 3- μm -thick undoped buffer layer was sandwiched between the quaternary layer and the substrate. The LPE growth was carried out using a two-phase solution technique described in the paper reported by Arai *et al.*¹⁴ Zn was diffused into the heterostructure in an evacuated silica ampule at 600 °C employing a mixture of Zn_3P_2 and InP as the Zn source. The depth profiles of matrix elements were analyzed using the sputtering Auger electron spectroscopy (AES) with 3.5 keV Ar⁺ ion bombardment and recording the depth distribution of Ga (1067 eV), In (399 eV), As (1224 eV), and P (120 eV) peaks. The depth profiles of Zn, Ga, and As were also measured by secondary-ion mass spectrometry (SIMS) with a Cs⁺ beam (to detect Zn) and an O₂⁺ beam (to detect Ga and As) at Charles Evans and Associates, Redwood City, California. The absolute value of Zn concentration in the heterostructure was estimated from a comparison with the data from the Zn-implanted InP standards of known dose.

Figures 1(a) and 1(b) show AES depth profiles for the as-grown and Zn-diffused samples (600 °C, 1 h) of a $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ -InP heterostructure (2- μm -thick quaternary), respectively. There is little change in the profiles of P and As after Zn diffusion. In contrast, the In and Ga profiles are significantly changed in the whole LPE layer. We note that the In and Ga profiles are discontinuously changed at the interface, i.e., In is depleted on the right side and accumulated on the left side of the interface, while Ga is distributed with the opposite tendency. Furthermore, a considerable outdiffusion of Ga from the surface is observed.

The large difference in the intermixed depths of group III and V atoms is clearly confirmed also in the SIMS profiles for a 4 h, Zn-diffused sample (0.8- μm -thick quaternary) as shown in Fig. 2. The peak of Ga intensity at the interface is also identified in this sample; however, its abruptness is less noticeable because of the poor resolution of SIMS analysis for high concentration components. The results shown in Figs. 1(b) and 2 indicate that the Zn diffusion in this structure induces a predominant intermixing and redistribution of group III atoms, as observed in other systems such as InAlGaP-GaAs,⁵ InGaPAs-GaAs,⁷ and InGaAs-InP.^{15,16}

^{a)} Department of Electrical Engineering, Pohang Institute of Science and Technology, Pohang, Kyungbuk, Korea.

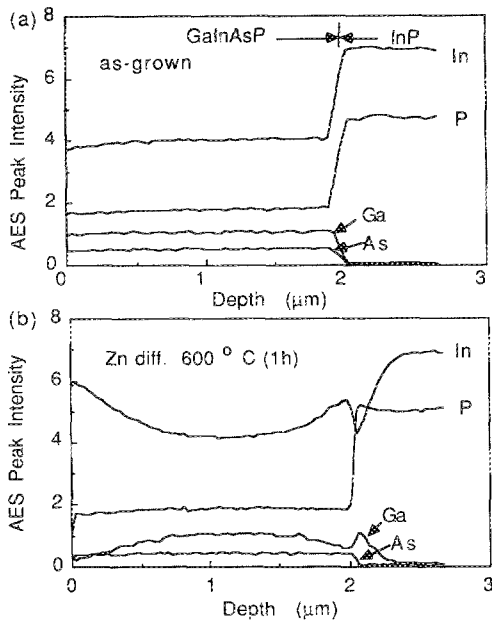


FIG. 1. AES profiles for (a) as-grown and (b) Zn-diffused (1 h, 600 °C) $\text{Ga}_{0.28}\text{In}_{0.72}\text{As}_{0.61}\text{P}_{0.39}\text{-InP}$ heterostructure. The Zn diffusion induces significant intermixing of group III atoms (In and Ga) showing discontinuous profiles at the interface, while the group V atoms (P and As) profiles are little changed.

The discontinuous interdiffusion profiles of In and Ga at the interface that appeared in Fig. 1(b) might be originated from a lattice-matching condition which should be significantly affected during the intermixing. Such distorted interdiffusion profiles have also appeared in the InAlGaP-GaAs ⁵ and InGaAs-InP ¹⁵ structures. While in the $\text{In}_x\text{Ga}_{1-y}\text{P}_y\text{As}_{1-y}\text{-GaAs}$ ($x = 0.06$, $y = 0.05$) heterostructure⁷ with In and P contents low enough that the change in lattice parameters of both layers during intermixing is negligible, the whole In profile showed a nearly complementary error function curve throughout the diffusion scale of $\sim 5 \mu\text{m}$ depth.

We try to explain our observed results with the existing models for Zn diffusion and IDEI in III-V compounds. The migration of group III atoms can be promoted if the $V_p\text{Zn}V_p$ complex moves through the exchange of a Zn atom and a neighboring In (or Ga) atom followed by a sequential migration of P (or As) vacancies as proposed by Yamada *et al.*¹³ In this process, however, the migration of P vacancies should be accompanied by a considerable intermixing of

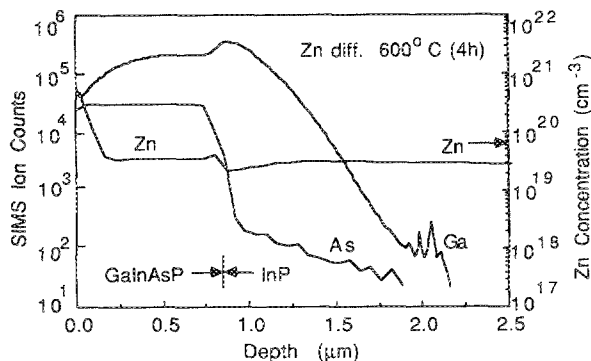
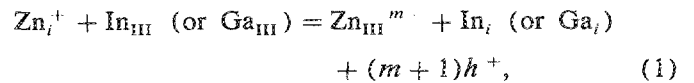


FIG. 2. SIMS profiles for Zn diffused (4 h, 600 °C) $\text{Ga}_{0.28}\text{In}_{0.72}\text{As}_{0.61}\text{P}_{0.39}\text{-InP}$ heterostructure. The large difference in the interdiffusion depths of group III and V atoms is clearly shown. Ga is accumulated near the interface and outdiffused from the surface.

group V atoms. In the original complex model,^{12,17} it has been supposed that the $V_p\text{Zn}V_p$ complex is immobile and that a diffusing species to transport Zn atoms is only an interstitial transited from the complex or other substitutionals. In this case also, the migration of group V atoms via P vacancies or P interstitials is essential for the formation and dissociation of the complex. Furthermore, the annealing condition under an overpressure of P given from the Zn_3P_2 source used in this study would suppress the formation of P vacancies needed for the $V_p\text{Zn}V_p$ complex. Therefore, we rule out the Zn complex models for the observed result in our diffusion system. From the observed insignificant anion interdiffusion, we also rule out other vacancy (single vacancy or divacancy) migration modes² through first nearest-neighbor hopping, as discussed in the previous works.^{7,15}

Therefore, we suggest that the cation interdiffusion in this structure would be enhanced by a similar interstitial migration process as proposed^{4,5,7} to explain the Zn DEI behavior in the GaAs-based alloys. The most likely mechanism to create the interstitials of host elements by Zn diffusion is a kick-out mechanism proposed by Gösele and Morehead,¹⁸ in which Zn_i occupy a cation site generating a cation interstitial as the following reaction^{4,7,18}:



where the subscripts *i* and III denote interstitials and cation sublattice sites, respectively, and *h* is a hole. Since a portion of Zn atoms appears to be acceptors in InP¹² and GaInAsP,¹⁹ we assume that the Zn_{III} exists as a neutral ($m = 0$) or a singly ionized ($m = 1$) isolated substitutional because of incomplete ionization.²⁰ In the statistical aspect, the value of *m* in reaction (1) may be taken as an average charge of the Zn_{III} in a local volume, which is $0 < m < 1$. The interstitial species, In_i and Ga_i , generated by this mechanism are expected to move rapidly from the quaternary layer, and then displace host atoms by the following reaction⁷:



For simplicity, the charge state of self-interstitials is assumed here to be neutral, even though the positively charged interstitials may be a dominant diffusing species under a *p*-type doping condition by the Fermi level effect.^{3,4} Depending on the charge states of Zn_{III} and self-interstitials, the number of holes involved in reaction (1) is varied.^{4,8} Further investigation on the electrical states of these species is required.

Based on the kick-out mechanism, we can analyze the relative diffusion rate of cation sublattices to Zn atoms. The mass action law for Eq. (1) with an assumption of $[h^+] = m[\text{Zn}_{\text{III}}]$ gives¹⁸

$$\begin{aligned} [\text{III}_i][\text{Zn}_{\text{III}}]^{m+2}/[\text{Zn}_i] \\ = [\text{III}_i]'[\text{Zn}_{\text{III}}]'^{m+2}/[\text{Zn}_i]' = \text{constant}, \end{aligned} \quad (3)$$

where III_i is cation interstitial, $[\]$ denotes concentration, and $[\]'$ denotes equilibrium concentration. Considering only the surface plateau region of the Zn profile where the whole interdiffusion is restricted as shown in Fig. 2, we simply assume that an equilibrium for the Zn and cation intersti-

tials is maintained in this region.^{10,18} Then the rates of the increase of Zn_{III} , Ga_{III} , and In_{III} concentrations are proportional to the flux gradient of each interstitial species if the diffusion coefficients of substitutional species are neglected, i.e., $\partial[Ga_{III}]/\partial t = D_{Ga} \partial^2[Ga_i]/\partial x^2$ as an example for Ga species.^{10,18} Combining Eq. (3) with these diffusion equations assuming $[III_i] = [III_i]'$ for Zn diffusion and $[Zn_i] = [Zn_i]'$ for group III interdiffusion, we obtain the ratio of effective diffusion coefficients of group III and Zn atoms:

$$\frac{D_{III}}{D_{Zn}} = \frac{1}{(m+2)} \frac{D_{III} [III_i]' [Zn_{III}]'^{2m+4}}{D_{Zn} [Zn_i]' [Zn_{III}]'^{2m+3} [III]'}, \quad (4)$$

where D_{III} and D_{Zn} are, respectively, diffusion coefficients of III_i and Zn_i , and $[III]$ is the total concentration of cation sublattices. This equation implies that D_{III}/D_{Zn} is proportional to D_{III}/D_{Zn} , and $[III_i]'/[Zn_i]'$, which may be the main factors dependent on matrix materials. In our system, D_{III}/D_{Zn} is estimated to be about 1/400 from the SIMS profiles of Ga in Fig. 2 and of Zn obtained from a 1 h, Zn-diffused sample (not shown) using the approximation of $D \approx x^2/t$, where x is the diffusion depth and t is the diffusion time. This value is much smaller than the data obtained in a $GaAs_{0.06}Ga_{0.94}P_{0.11}As_{0.89}$ heterostructure,²¹ which are between 1/15 and 1/10 at the temperature range of 650–730 °C. Such a low enhancement effect of Zn on cation interdiffusion in the InP-based structure may be attributed to a relatively small value of D_{III}/D_{Zn} , or $[III_i]'/[Zn_i]'$ in this system. The Zn DEI behavior in real systems should be more complex than the assumptions leading to Eq. (4). Since the III_i (or III_i') would be supersaturated in the Zn-diffused region, a recombination process of III_i with sublattice sites may control the interdiffusion.⁴ Furthermore, a large stress induced by intermixing near the interface will cause a local failure of the normal diffusion kinetics dependent on the concentration gradient, as indicated in Fig. 1 (b), and could suppress the advance of intermixing.

In summary, the relative enhancement effect on group III and V sublattices due to Zn diffusion was determined in a $GaInAsP$ -InP heterostructure. Predominant enhancement on group III interdiffusion is observed by the Zn diffusion with a P-rich source, and is not consistent with the expectation from the $V_p Zn V_p$ complex model. This result is in

agreement with a kick-out mechanism, and suggests that the Zn diffusion in InP- and InP-related alloys is controlled by cation interstitials rather than anion vacancies under a group-V-rich diffusion condition. A local disturbance of concentration gradient dependent interdiffusion is observed at the mixed interface, which may be due to an interfacial stress induced by intermixing.

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- ¹W. D. Laidig, N. Holonyak, Jr., M. D. Camras, K. Hess, J. J. Coleman, P. D. Dapkus, and J. Bardeen, *Appl. Phys. Lett.* **38**, 776 (1981).
- ²J. A. Van Vechten, *J. Appl. Phys.* **53**, 7082 (1982).
- ³T. Y. Tan and U. Gösele, *J. Appl. Phys.* **61**, 1841 (1987).
- ⁴T. Y. Tan and U. Gösele, *Appl. Phys. Lett.* **52**, 1240 (1988).
- ⁵D. G. Deppe, D. W. Nam, N. Holonyak, Jr., K. C. Hsieh, J. E. Baker, C. P. Kuo, R. M. Fletcher, T. D. Osentowski, and M. G. Craford, *Appl. Phys. Lett.* **52**, 1413 (1988).
- ⁶D. G. Deppe, W. E. Plano, J. E. Baker, N. Holonyak, Jr., M. J. Ludowice, C. P. Kuo, R. M. Fletcher, T. D. Osentowski, and M. G. Craford, *Appl. Phys. Lett.* **53**, 2211 (1988).
- ⁷H.-H. Park, K. H. Lee, and D. A. Stevenson, *Appl. Phys. Lett.* **53**, 2299 (1988).
- ⁸D. G. Deppe and N. Holonyak, Jr., *J. Appl. Phys.* **64**, R93 (1988).
- ⁹R. L. Longini, *Solid-State Electron.* **5**, 127 (1962).
- ¹⁰B. Tuck and M. A. H. Kadhim, *J. Mater. Sci.* **7**, 585 (1972).
- ¹¹M. E. Greiner and J. F. Gibbons, *Appl. Phys. Lett.* **44**, 750 (1984).
- ¹²B. Tuck and A. Hooper, *J. Phys. D* **8**, 1806 (1975).
- ¹³M. Yamada, P. K. Tien, R. J. Martin, R. E. Nahory, and A. A. Ballman, *Appl. Phys. Lett.* **43**, 594 (1983).
- ¹⁴S. Arai, Y. Suematsu, and Y. Itaya, *IEEE J. Quantum Electron.* **QE-16**, 197 (1980).
- ¹⁵K. Nakashima, Y. Kawaguchi, Y. Kawamura, Y. Imamura, and H. Asahi, *Appl. Phys. Lett.* **52**, 1383 (1988).
- ¹⁶S. A. Schwarz, P. Mei, T. Venkatesan, R. Bhat, D. M. Hwang, C. L. Schwartz, M. Koza, L. Nazar, and B. J. Skromme, *Appl. Phys. Lett.* **53**, 1051 (1988).
- ¹⁷P. K. Tien and B. I. Miller, *Appl. Phys. Lett.* **34**, 701 (1979).
- ¹⁸U. Gösele and F. Morehead, *J. Appl. Phys.* **52**, 4617 (1981).
- ¹⁹G. J. van Gurp, D. L. A. Tjaden, G. M. Fontijn, and P. R. Boudewijn, *J. Appl. Phys.* **64**, 3468 (1988).
- ²⁰N. Chand and P. A. Houston, *J. Electron. Mater.* **11**, 37 (1982).
- ²¹H.-H. Park, B. K. Kang, K. H. Lee, and D. A. Stevenson (unpublished work).