Defect formation and dopant diffusion in III–V semiconductors: zinc diffusion in GaP

Defect formation and dopant diffusion in III–V semiconductors: zinc diffusion in GaP

Christian Jäger and Wolfgang Jäger

Centre for Microanalysis, Faculty of Engineering, Christian-Albrechts-University, Kaiserstraße 2, D-24143 Kiel, Germany

Abstract
Using zinc diffusion as a model case, the generation and role of extended defects formed in GaP single crystals during dopant diffusion at elevated temperatures have been investigated extensively by methods of analytical transmission electron microscopy of cross-section specimens. The temporal evolution of the defect structure and the anomalous shapes of the zinc concentration profiles are dependent upon the chosen diffusion parameters. A comparison with results for GaSb and GaAs indicates that types, formation processes and many aspects of the temporal evolution of the diffusion-induced defects represent general phenomena for III–V semiconductors under high-concentration dopant diffusion.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Diffusion of Zn into III–V compound semiconductors is frequently used for p-type doping for electronic and optoelectronic devices. Zinc diffusion in gallium phosphide which occurs via an interstitial–substitutional exchange mechanism is relatively fast compared to the self-diffusion in this material [1]. Earlier investigations for GaAs have shown that the analysis of extended defects formed by dopant diffusion may yield important information about the role of point defects during diffusion and the influences of the extended defects on dopant diffusion and resulting diffusion profiles [2–6]. Investigations of Zn dopant diffusion anneals in GaP crystals containing an initially large number of defects revealed no significant effects on the microstructure [7]. In an effort to understand the formation of extended defects during dopant diffusion in virtually defect-free GaP single crystals (dislocation density $<10^5$ cm^{-2}), we have performed detailed studies using zinc diffusion from the vapour phase under various ambient conditions as a model case for the interstitial–substitutional diffusion of dopant atoms. The diffusion anneals were carried out in quartz ampoules at temperatures between 900 and 1100 °C and for diffusion times up to 17 h using elemental Zn and P at different weight ratios as diffusion sources. The diffusion-induced formation and evolution of extended defects have
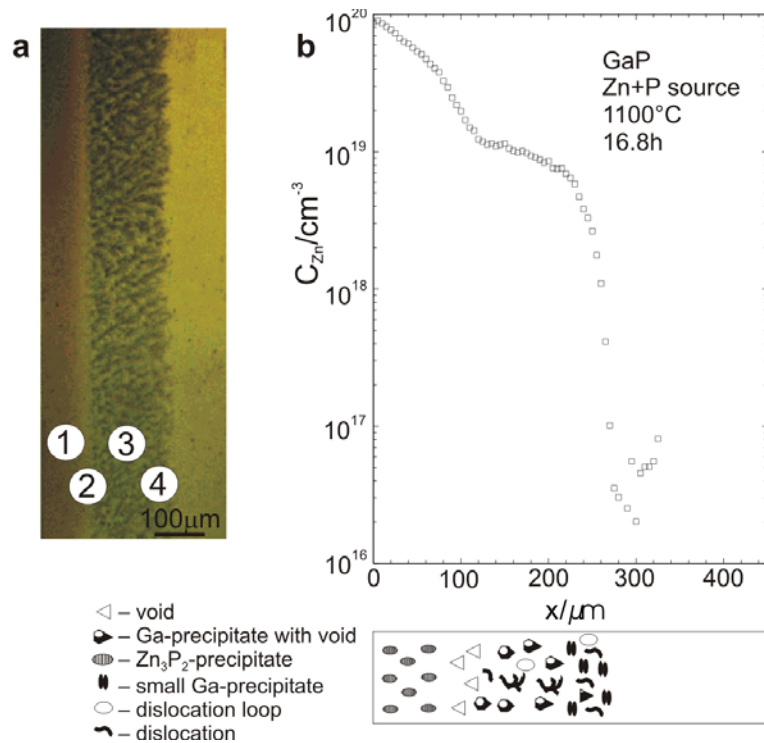
Figure 1. (a) A light microscopy transmission image of a GaP sample diffused at 1100 °C for 16.8 h. (b) The corresponding Zn concentration profile as measured by SIMS and arrangements of diffusion-induced defects.

been investigated by transmission electron microscopy (TEM) of cross-section samples using an analytical Philips CM30 transmission electron microscope at 300 kV. This paper summarizes the most important results of these investigations and compares the results with studies of zinc diffusion into GaSb, GaAs and InP [3, 4, 6, 12–14].

2. Formation of defects and relationship to concentration profiles

The relationship between the diffusion-induced defect structure in GaP and the zinc concentration profiles measured by means of secondary-ion mass spectroscopy (SIMS) is illustrated by figure 1(b) for the case of Zn diffusion under P-rich conditions at 1100 °C. Typical of the large partial pressures of P during ampoule diffusion is the two-step concentration profile, $C_{Zn}(x)$, consisting of a diffusion front region with a steep decrease at the maximum penetration depth of 260 μm and a high-concentration surface region with a second step at 95 μm. Anomalous Zn diffusion profiles are also observed for lower partial pressures of P (P-poor diffusion conditions), leading on for longer diffusion times to box-shaped Zn concentration profiles characterized by only one plateau and one step (not shown) [12, 13]. The surface values of C_{Zn} range between about 10^{19} and 10^{20} cm^{-3}, and the maximum penetration depths increase with increasing Zn weight fraction in the diffusion ampoule for a chosen diffusion time.

Structural investigations by transmission electron microscopy of cross-section specimens and by light microscopy in transmission show that the diffusion of zinc into GaP generates extended defects throughout the diffused regions. Beyond the diffusion front the crystal

remains free of extended defects. The defect varieties and distributions constitute a complicated picture and are subject to temporal evolution and to the diffusion conditions. The light microscopic image reveals dark absorption areas which are associated with dislocations and metallic precipitates [11] of the front region of the diffusion profile (figure 1(a)). Such distinct areas are absent in the surface region, which shows a colour different from that of the non-diffused GaP matrix. The distribution of different types of defect as obtained from the TEM investigations, the absorption contrast and the Zn concentration profile reflect the clear spatial correlation (figures 1(a), (b)). The diffusion front regions show arrangements of perfect dislocation loops (diameters up to 750 nm), small precipitates in spatial correlation with the loops, dislocations and precipitates with a void volume. Under the applied P-rich diffusion ambient conditions, the surface region is composed of voids and of small Zn-rich precipitates, and few dislocations are observed. For P-poor zinc diffusion (box-shaped profiles, not shown), the surface regions maintain largely the structure also observed for the diffusion front regions.

The zinc diffusion into GaP from strong diffusion sources generates in the front regions extended defects in the form of dislocations and Ga precipitates in voids. Using different methods for the loop type analysis [8, 11] the dislocation loops formed in different depth regions within the diffusion zone are identified as being of interstitial type, with {110}-habit planes and Burgers vectors of the type $(a/2)\langle 110\rangle$. Such interstitial loops which do not comprise a stacking fault are likely to include an extra layer containing both Ga and P. Precipitate compositions were deduced from energy-dispersive x-ray microanalyses at 250 kV, analysing Zn-Kα, Ga-Kα and P-Kα spectrum lines. These analyses show that the precipitates with voids consist predominantly of Ga. The types of defect produced in the diffusion front regions of the crystals are similar to those observed during Zn diffusion in GaAs [3, 6]. The void/Ga precipitate sizes and the precipitate-to-void volume change with increasing diffusion time. Typical of later stages of defect formation near the diffusion front in GaP is the inhomogeneous spatial arrangement of defects consisting of dislocation networks and planar arrays of precipitates (figure 3(a)). Similar to what was observed for GaAs [3, 6] and for InP [14], our observations of dislocation networks can be understood as the result of entanglement of loops during growth, and the formation of arrays of precipitates as a result of dislocation climb induced by the diffusion-induced formation and absorption of Ga interstitials. As an example of the effects of zinc diffusion at the diffusion front of single-crystalline GaSb, figure 3(b) shows the stage of loop formation followed by loop growth and dislocation entanglement. These microscopic observations of loop growth and of dislocation climb indicate that the extended defects formed initially are effective Ga self-interstitial sinks and are able to provide a path to establishing defect-mediated local point defect equilibria.

3. Temporal evolution of the defect structure

The temporal evolution of the defect structure and the anomalous shapes of the zinc diffusion profiles are dependent upon the diffusion ambient conditions. Except for a crystal region close to the initial surface which is largely free of defects, significant differences are observed for the surface regions both as regards the dislocation structure (figure 3) and, especially, for the void/precipitate structure (figures 2(b), (c)). For P-poor diffusion conditions, Ga precipitates with voids have an essentially constant precipitate-to-void volume ratio throughout the zinc-diffused regions. Hence, the Zn diffusion creates crystal regions in contact with gallium which is liquid at the diffusion temperatures. Spatially resolved x-ray microanalyses show that the precipitates closer to the surface also contain Zn, whose volume fraction increases with decreasing distance to the surface. In combination with this segregation of zinc to Ga precipitates, the precipitate structure coarsens slightly during the diffusion anneals [12].
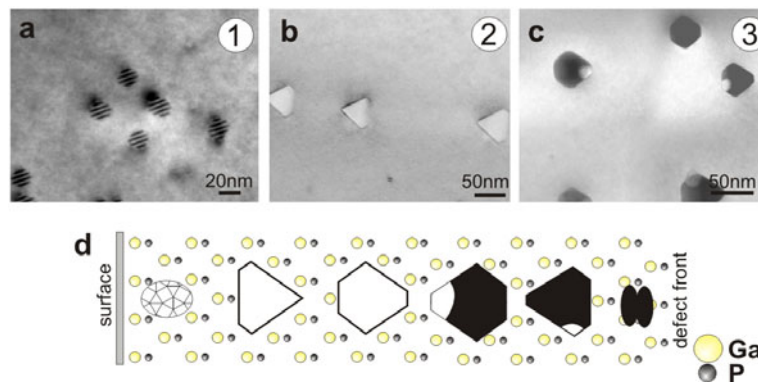
Figure 2. (c) Ga precipitates with voids, (b) faceted voids and (a) precipitates displaying Moiré fringe contrast; bright-field TEM micrographs taken in the profile areas numbered correspondingly in figure 1(a). (d) Temporal evolution of the diffusion-induced precipitate structure for P-rich diffusion conditions and the morphology of voids and Ga precipitates with voids (schematic diagram).

Characteristic for zinc diffusion including the group V element P in the vapour phase are the formation of voids from Ga precipitates and their complete dissolution during the diffusion anneals (figures 2(a)–(d) and 1(b)). The Ga precipitates with voids and the voids are faceted on {111} and {001} planes. For longer diffusion times, the voids assume the shape of nearly perfect tetrahedra. From the asymmetry of the contrast of high-odd-index Bragg lines in {002} dark-field LACBED patterns, the relationship between void faceting and crystal polarity has been deduced—yielding information about the possible atomic surface terminations of the interfaces [9, 10]. These investigations suggest that the large {111} void facets are terminated by Ga atoms. Independently of the diffusion conditions, the crystal regions near the wafer surface show the presence of Zn in precipitates. The nature of the crystalline precipitates (figure 2(a)) has been determined as a cubic Zn_3P_2 phase by combining x-ray microanalyses, measurements of the lattice parameters from Moiré fringe distances and electron diffraction analyses [12]. Figure 2 shows examples of the different kinds of precipitate which are formed by zinc diffusion in GaP: Ga precipitates with voids in the front region, voids in the transition region and crystalline precipitates in the surface region. The temporal evolution of the precipitate structure and the morphology of the Ga precipitates and voids in GaP is summarized schematically in figure 2(d) for diffusion under P-rich diffusion conditions.

4. Summary and conclusions

The formation and role of extended defects formed in the single-crystalline III–V compound semiconductors GaP and GaSb during Zn dopant diffusion at elevated temperatures have been investigated extensively by methods of analytical TEM and compared with measurements of concentration profiles [11–13, 15]. The most important results and conclusions may be summarized as follows:

- Diffusion of zinc from strong diffusion sources generates extended defects in the form of dislocations and Ga precipitates in voids in initially defect-free crystal regions at a sufficiently large distance from the crystal surfaces. The formation of defects in GaP may be explained on the basis of the model suggested earlier for defect formation in GaAs [3].
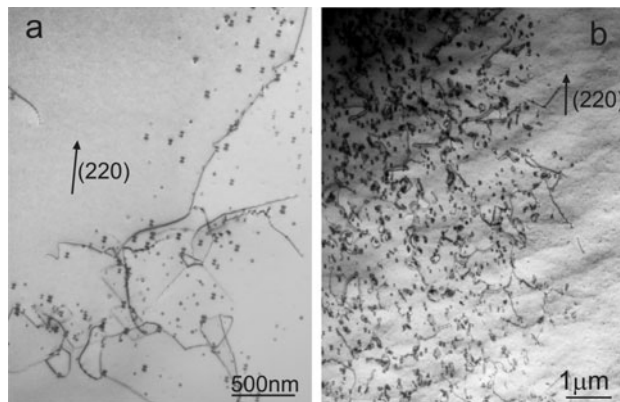
Figure 3. (a) Dislocation loops and a network of dislocations with loops and precipitates in GaP; a TEM bright-field micrograph taken in region 4 (figure 1(a)). (b) Dislocation loops, a network of dislocations and precipitates in GaSb near the diffusion front (Sb-rich diffusion at 610 °C, 24 h).

The model assumes that defect formation results from the local supersaturations of point defects created by incorporation of zinc into gallium sublattice sites via the kick-out mechanism, because the transport of Ga interstitial atoms to the crystal surface or into deeper crystal regions is apparently not fast enough at the diffusion temperature. Since Ga interstitial atoms are mobile at the diffusion temperature, they agglomerate and form dislocation loops. In order to avoid an energetically unfavourable stacking fault and to maintain stoichiometry, phosphorus atoms which are provided by emission of phosphorus vacancies in initially defect-free crystals have to be incorporated into the loop. Mobile phosphorus vacancies agglomerate and form voids with gallium precipitates which then may act as sinks for further Ga interstitials created during the Zn diffusion.

- The microscopic observations of effective loop growth and of dislocation climb confirm that the extended defects formed initially are effective Ga self-interstitial sinks and are able to provide a path to establishing defect-mediated local point defect equilibria. The results for zinc diffusion in GaSb (figure 3(b)) may be explained in an analogous way.

- The temporal evolution of the defect structure and the anomalous shapes of the zinc diffusion profiles are dependent upon the diffusion parameters (see also [1, 12, 13]). Characteristic for Zn diffusion sources including the group V element P in the vapour phase are the formation of voids from Ga precipitates and—at a later stage—the complete dissolution of voids, indicating that an effective outdiffusion of Ga atoms occurs and that the near-surface crystal regions are turned into an effective sink for gallium. Characteristic for Zn diffusion with the group V element P being largely absent in the vapour phase are the observations of Zn segregation to Ga precipitates. Obviously, the Ga transport is retarded under such conditions. These results of our present study are in good agreement with diffusion experiments performed for GaAs with different source compositions at similar homologous temperatures ($T/T_m \approx 0.8$, $T_m =$ melting temperature) and confirm earlier conclusions [4, 6]. Similar to the case for GaAs [4], the fundamental physical reason leading to this situation is that, under the P-rich ambient conditions, the Zn and P partial pressures constitute two competing thermodynamic driving forces for producing GaP crystals with two extreme compositions: zinc for Ga-rich crystals and phosphorus for P-rich crystals. During Zn indiffusion, a Ga-rich crystal in contact with liquid Ga in voids is produced first, with a high effective diffusivity of the Zn substitutional species via the kick-out mechanism and an accelerated Zn indiffusion for high Zn partial pressure.

Further Zn incorporation onto the Ga sites ceases to be effective later on in the near-surface region, which allows the crystal to become rich in P under P-rich ambient conditions with a lower effective diffusivity of Zn. Therefore, for GaP also the two-step profiles may be interpreted as a superposition of two box-like profiles with Zn solubilities and effective diffusivities which are different for the Ga-rich and the P-rich crystal regions.

- Characteristic for crystal regions with high Zn concentrations are the presence of Zn-rich precipitate phases, such as crystalline Zn_3P_2, and that of a near-surface defect structure which shows a complex dependence on the diffusion conditions [12]. The formation of voids and also the formation of crystalline Zn_3P_2 precipitates are clear indications that supersaturations of interstitial Ga atoms do not play a role any more in the crystal surface regions.

In summary, the comparison with results for GaAs [4, 6] indicates that types and formation processes as well as many aspects of the temporal evolution of the diffusion-induced defects represent general phenomena for III–V semiconductors under high-concentration dopant diffusion. The presence of these defects and their modification indicate that the GaP crystal establishes, during the temporal evolution, locally different point defect equilibria and thereby influences the further Zn diffusion, depending on the conditions. During Zn indiffusion, Ga-rich crystal regions in equilibrium with the liquid Ga and the vapour phase within the voids are produced first, thereby holding the Ga interstitial and P vacancy concentrations close to the appropriate thermal equilibrium values for a Ga-rich GaP crystal. For longer diffusion times the Zn-diffused crystal regions try to achieve equilibrium: defects take on equilibrium shapes or undergo modifications. These investigations contribute to our understanding of the anomalous shapes of Zn diffusion profiles of III–V compound semiconductors and yield important information for the modelling of dopant diffusion, including that for weak-source diffusion conditions in which no defects are observed [6, 15, 16].

Acknowledgments

References

[1]   Tuck B 1995 *Atomic Diffusion in III–V Semiconductors* (Bristol: Hilger)
[2]   Tan T Y, Gösele U and Yu S 1991 *Crit. Rev. Solid State Mater. Sci.* **17** 47
[3]   Luysberg M, Jäger W, Urban K, Schänzer M, Stolwijk N A and Mehrer H 1992 *Mater. Sci. Eng.* B **13** 137
[4]   Jäger W, Rucki A, Urban K, Hettwer H G, Stolwijk N A, Mehrer H and Tan T Y 1993 *J. Appl. Phys.* **74** 4409
[5]   Bösker G, Stolwijk N A, Hettwer H G, Rucki A, Jäger W and Södervall U 1995 *Phys. Rev.* B **52** 927
[6]   Rucki A and Jäger W 1997 *Defect Diffus. Forum* **143** 1095
[7]   Ball R K and Hutchinson P W 1980 *J. Mater. Sci.* **22** 2376
[8]   Jäger Ch, Spiecker E, Morniroli J P and Jäger W 2002 *J. Phys.: Condens. Matter* at press
[9]   Jäger Ch, Spiecker E, Morniroli J P and Jäger W 2002 *Ultramicroscopy* **92** 273
[10] Spiecker E 2002 *Ultramicroscopy* **92** 111
[11] Jäger Ch 2002 *Dissertation* University of Kiel
[12] Jäger Ch, Jäger W, Pöpping J, Bösker G and Stolwijk N A 2000 *J. Electron Microsc.* **48** 1037
[13] Jäger Ch, Jäger W, Bösker G, Pöpping J and Stolwijk N A 2000 *Phil. Mag.* A **80** 1
[14] Wittorf D, Rucki A, Jäger W, Dixon R H, Urban K, Stolwijk N A, Hettwer H G and Mehrer H 1995 *J. Appl. Phys.* **77** 2843
[15] Jäger C, Jäger W, Pöpping J, Stolwijk N A and Södervall U 2001 *Defect Diffus. Forum* **194–199** 731
[16] Pöpping J, Stolwijk N A, Södervall U, Jäger C and Jäger W 2001 *Physica* B **308** 895