Phosphorus and antimony in GaAs as tracers for self-diffusion on the arsenic sublattice

R. F. Scholz a) and U. Gösele
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

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For investigating arsenic self-diffusion, phosphorus (P) and antimony (Sb) were used. New P and Sb in-diffusion experiments show the same behavior as P and Sb interdiffusion experiments. This is in contradiction to results from the literature. By means of transmission electron microscopy we observed a phase transformation to polycrystalline GaAs_{1-x}P_x at the surface under experimental conditions similar to those described in the literature. This leads to a penetration depth much higher than for the P in-diffusion without this phase transformation. The new diffusion coefficients of the P and Sb in-diffusion above 900 °C are in the same range as the interdiffusion coefficients and self-diffusion coefficients from As-tracer diffusion. From this result we conclude that P and Sb have tracer properties for arsenic self-diffusion in GaAs. Measurements of the diffusion coefficients at different As-vapor pressures revealed that As self-diffusion is dominated by As self-interstitials. Furthermore, we performed annealing experiments on differently doped samples. There is no indication of a Fermi-level effect. Hence, As self-diffusion is governed mainly by neutral defects. Between 900 and 1100 °C, we obtain an Arrhenius expression \( D = 75 \exp(-4.4 \text{ eV/kT}) \text{cm}^2/\text{s}, \) which describes As self-diffusion. The P in-diffusion values below 900 °C show a weaker temperature dependence, which indicates a changeover to a different diffusion mechanism. © 2000 American Institute of Physics. [S0021-8979(00)06601-9]

I. INTRODUCTION

In the last few years, several investigations dealt with the diffusion on the arsenic sublattice in GaAs. 1–6 Many experiments on self-diffusion of gallium (Ga) had already been performed because the important dopants beryllium (Be), zinc (Zn), and silicon (Si) are mainly dissolved on the Ga sublattice. 7–9 The arsenic self-diffusion has become a topic of interest since carbon is used as a p-type dopant. Carbon is dissolved on the arsenic sublattice and has a much lower diffusion coefficient than Be or Zn. 10 In order to achieve improved crystal properties, postannealing steps after crystal growth are frequently necessary. 11,12 For this procedure, knowledge of the arsenic diffusion parameters and understanding of the relevant diffusion mechanisms are important. There are also some new applications of sulfur as a n-type dopant in transistor devices. 13,14 Sulfur is dissolved on the arsenic sublattice and has a complex diffusion behavior, which is influenced by the diffusion of native point defects on the arsenic sublattice. 1

Up to some years ago, only few investigations had been reported on arsenic self-diffusion based on the radioactive As-isotope 73As. 15,16 Therefore, Egger et al. 2 investigated P and Sb interdiffusion of GaAs/GaAs_{1-x}P_x and GaAs/GaAs_{1-x}Sb_x heterostructures. These experiments were based on the hope that P and Sb may have diffusion properties similar to those of As in GaAs. This concept had already been used for the Ga sublattice. Here GaAs/AlAs heterostructures were used successfully to study Ga self-diffusion in GaAs. 17–19 In Fig. 1, the diffusion coefficients from older self-diffusion experiments on the arsenic sublattice 15,16 are compared with P and Sb interdiffusion coefficients 2–4 and P in-diffusion data. 20 As pointed out by Schultz et al. 3 the P and Sb interdiffusion data show the same values as the former arsenic self-diffusion data from Palfrey et al. 16 Furthermore, the interdiffusion profiles have equilibrium character, which means they can be described by a constant diffusion coefficient. From this, Schultz et al. 3 concluded that P and Sb have tracer properties for arsenic diffusion and can be used to determine arsenic self-diffusion in GaAs. Experiments using different arsenic vapor pressures showed diffusion coefficients that increased with increasing arsenic vapor pressure for both P and Sb interdiffusion. Throughout this article this will be called a positive pressure dependence. If the diffusion coefficient decreases with increasing arsenic vapor pressure, it will be called a negative pressure dependence. Schultz et al. 3 discussed in detail the possible diffusion mechanisms in GaAs and the dependence on the arsenic vapor pressure. For both the P and Sb interdiffusion, the equilibrium shape of the profiles and the positive pressure dependence lead to the conclusion that an interstitial-substitutional mechanism governs P and Sb interdiffusion. This means the Frank–Turnbull mechanism 21 and/or the kick-out mechanism 22 dominate the diffusion process. Under equilibrium conditions of the native point defects as for the P and Sb interdiffusion, it is not possible to separate the two mechanisms. Therefore, it is not possible to decide unambiguously whether As self-diffusion is governed by arsenic vacancies or arsenic self-interstitials. However, the observation that the coefficients of As self-diffusion and P and Sb...
interdiffusion are in the same range the positive pressure dependence lead to the assumption that

\[
\frac{D_{iP}c_{iP}^{eq}}{c_{iP}^{eq}} \approx \frac{D_{SB}c_{SB}^{eq}}{c_{SB}^{eq}} \approx \frac{D_{iAs}c_{iAs}^{eq}}{c_{0}}.
\]

(1)

Sulfur in-diffusion experiments\(^1\) and investigations of arsenic precipitation distribution after postgrowth annealing steps\(^11,12\) confirm this statement. Hence, Schultz et al.\(^3\) postulated that As self-diffusion is dominated by arsenic self-interstitials.

These results are in contradiction to previous experiments by Palfrey et al.,\(^16\) who in radioactive \(^7\)As tracer in-diffusion experiments have proven a negative pressure dependence. Hence, they concluded that the vacancy mechanism dominates the arsenic self-diffusion

\[
\text{As}_{\text{As}} + \text{V}_{\text{As}} \rightarrow \text{V}_{\text{As}} + \text{As}_{\text{As}}
\]

(2)

\(\text{As}_{\text{As}}\) are the arsenic lattice atoms, and \(\text{V}_{\text{As}}\), the arsenic vacancies. Another problem is the P in-diffusion data by Jain et al.,\(^20\) which are several orders of magnitude higher than the arsenic self-diffusion data and the P interdiffusion ones (Fig. 1). These data have also a negative pressure dependence, shown in Fig. 1. These contradictions encouraged us to perform novel P and Sb in-diffusion experiments discussed in this article.

II. EXPERIMENTS

For the experiments, material was used, which had been grown by the vertical Bridgman technique and which showed a low dislocation density (etch pits/cm\(^2\)<10\(^4\)). Using this material avoids effects due to pipe diffusion on grown-in dislocations in the in-diffusion profiles.

The annealing experiments were performed in closed quartz ampoules. For this, the quartz ampoules were cleaned via RCA1 and RCA2 cleaning procedures as described in the literature.\(^23\) Before the sample was introduced into the quartz ampoule, the GaO-layer on the surface was removed by dipping the sample in concentrated HCl acid for 1 min. In order to establish a defined arsenic vapor pressure and defined P and Sb concentrations over the sample, pure metallic ingre-

\[
\text{As}_4, \text{P}_4, \text{and Sb}_4 \text{molecules dominate the gas phase (see literature on As,}^{24} \text{P,}^{25} \text{and Sb}^{26}\text{). The ampoule was attached to a vacuum system and pumped down below 10\(^{-5}\) mbar, before the sample and the ingredients were sealed. The volume in the ampoules after the sealing procedure was 6 cm\(^3\). The annealing was performed in a box furnace with a temperature controller allowing a relative accuracy better than \(\pm 1\) K. The overall temperature accuracy at the sample position was better than \(\pm 5\) K. After the annealing the ampoule was quenched in water.

For temperatures lower than 1000 °C we annealed differently doped samples to investigate the Fermi-level effect, which occurs if charged defects are involved in the diffusion process.\(^7\) After Blakemore,\(^27\) the intrinsic carrier concentration at 1000 °C is 1.5 \times 10\(^{17}\) cm\(^{-3}\). For our investigations we used Si doped samples \((n=1 \times 10^{18} \text{cm}^{-3})\), Zn doped ones \((p=1.5 \times 10^{19} \text{cm}^{-3})\) and undoped ones \((n\leq 5 \times 10^{13} \text{cm}^{-3})\). Therefore, below 1000 °C a Fermi-level effect should be measurable in these three types of samples, provided that charged point defects are involved in the arsenic self-diffusion process.

To characterize the defect formation during the in-diffusion we used cathodoluminescence (CL) images as described in Ref. 4. For the characterization by transmission electron microscopy (TEM) we have used a high-voltage JOEL 1000 microscope. The in-diffusion profiles were measured via secondary ion mass spectroscopy (SIMS) with a CAMECA 4ims-f device.\(^28\) Before measuring the samples via SIMS we cleaned them with a clean room tissue. The necessity of this procedure will be described later.

III. PHOSPHORUS IN-DIFFUSION WITH PHASE TRANSFORMATION

Jain et al.\(^20\) have used very high P vapor pressures (>30 bar) in their in-diffusion experiments. In our first experiments, we have used P vapor pressures between 1 and 8.5 bar, resulting in a phase transformation to polycrystalline GaAs\(_{1-x}\)P\(_x\), as shown in Fig. 2. The formation of a polycrystalline phase is not astonishing, since the lattice mis-

FIG. 2. TEM bright-field image of a sample annealed at 900 °C for 3 h, \(p_{\text{As}}=1\) bar and \(p_{\text{P}}=3\) bar. The formation of a polycrystalline GaAs\(_{1-x}\)P\(_x\) phase is illustrated.
match between GaAs and GaP is quite high (3.5%). The P content in the polycrystalline region determined by energy dispersive x-ray diffraction is about 30% (x~0.6). The SIMS profiles, obtained from these samples, do not allow a quantitative analysis because the SIMS signal is influenced by the strong change in the composition of the matrix. Therefore, we can get only a rough estimation of the penetration depth $x_p$. Via the following equation we calculated diffusion coefficients, which, however, do not represent the diffusion coefficients of defect-free GaAs

$$D = \frac{x_p^2}{2t}. \quad (3)$$

Figure 3 presents these diffusion coefficients together with the data of Jain et al.\textsuperscript{20} It is obvious that for P vapor pressures $\geq 1$ bar, high diffusion coefficients were achieved similar as in the old experiments. At 1000 °C we performed four experiments at different arsenic vapor pressures and a constant P vapor pressure of 8.5 bar. As we can further see from Fig. 3, these values tentatively indicate a positive pressure dependence, but due to the polycrystalline GaAs$_{1-x}$P$_x$ phase forming, it is not possible to determine the As pressure dependence reliably.

A possible phase transformation to GaP during the P in-diffusion was pointed out in a previous article.\textsuperscript{29} After Zn in-diffusion in GaAs, together with the presence of a high P vapor pressure, formation of a polycrystalline phase at the surface was observed, too.\textsuperscript{30}

We conclude that the former data by Jain et al.\textsuperscript{20} do not yield the P-diffusion coefficients in defect-free GaAs. Under the described experimental conditions, the formation of a polycrystalline GaAs$_{1-x}$P$_x$ phase increases the penetration depth of P in GaAs due to pipe diffusion along dislocations and grain boundaries. This is the reason why the diffusion coefficients calculated based on Eq. (3) are several orders of magnitude higher than the true diffusion coefficients of P in GaAs.

For measuring the real diffusion coefficients experimental conditions are required which prevent the formation of GaAs$_{1-x}$P$_x$ at the surface. As pointed out in Ref. 4, even for low P vapor pressures of 0.08 bar a misfit dislocation network occurred at the surface if no additional arsenic was added to the ampoule. CL images and TEM investigations revealed that the formation of extended defects at the surface were prevented, when P vapor pressures of 0.08 bar and arsenic vapor pressures of 0.1 bar at 900 °C and 0.2 bar at 1100 °C were used.

IV. IN-DIFFUSION WITHOUT PHASE TRANSFORMATION

A. Phosphorus in-diffusion in GaAs

For conditions with no phase transformation occuring we performed annealing experiments at various temperatures and arsenic vapor pressures. As shown in Fig. 4, the obtained profiles have a concave shape. Some profiles can be described by simulations with a kick-out mechanism under nonequilibrium conditions (Fig. 4). Such profiles, which were also obtained for Sb in-diffusion, are the reason that a coupled diffusion mechanism had been postulated in former articles.\textsuperscript{2,31} For the P and Sb interdiffusion the Frank–Turnbull mechanism was postulated with a positive arsenic pressure dependence, whereas for the in-diffusion experiments a vacancy mechanism was supposed with a negative arsenic pressure dependence. This is, however, in contradiction to the statement of Schultz et al.\textsuperscript{3} that P and Sb have tracer properties for the arsenic diffusion in GaAs. Tracer diffusion should not produce nonequilibrium concentrations of native point defects as indicated by the profiles in Fig. 4. As shown in the second SIMS measurement in Fig. 4, the profiles are not reproducible. Sometimes even two steps occur in the tail of the profile. The profiles at different temperatures cannot be explained by a closed set of simulation parameters.

To investigate lateral element distributions three-dimensional SIMS measurements were performed in the CAMECA 4ims-f system, where the data were measured in a scanning mode. For the standard one-dimensional SIMS profiles the scanning points of one sputtered layer are integrated into one data point. If all scanning points are recorded separately in a data file a three-dimensional element distribution is achieved. In Fig. 5 two layers of such a three-dimensional

![Fig. 3. Recent diffusion coefficients obtained after estimation via the mean penetration depth [Eq. 3], $p_{As} = 1$ bar. At 1000 °C four annealing experiments were performed for $p_{As}$ varying and $p_{P} = 8.5$ bar. The values of $p_{As}$ in [bar] are given beside the data points.](http://jap.aip.org/jap/copyright.jsp)

![Fig. 4. P in-diffusion profiles after annealing at 900 °C for 72 h and simulation via the kick-out mechanism under nonequilibrium conditions of the As self-interstitials. The second SIMS measurement was performed on the same sample, showing a step in the profile.](http://jap.aip.org/jap/copyright.jsp)
measurement are plotted. Lateral inhomogeneous areas are shown in the middle of the images. The bright edges are a typical SIMS effect. At the edges of the SIMS crater a diffusion takes place from the sample surface with the highest P concentration in the SIMS crater. The depth behavior of the three marked areas is quite different. In area (a) the P concentration is low already at a depth of 100 nm. While in area (c) the P concentration is still high at a depth of 250 nm, in area (b) there is a concentration step between the two layers. The laterally inhomogeneous concentration is due to P-containing particles on the surface. During quenching the ampoules, the P vapor can precipitate on the sample surface and form such P-containing particles, which are introduced into the crater during sputtering, causing one or more steps in the tail of one-dimensional SIMS profiles. To avoid this inhomogeneous concentration distribution we have tried to clean the surface by different methods. After cleaning of the surface by wiping it with a clean room tissue the inhomogeneous spots on the surface vanished. In Fig. 6 two SIMS profiles are plotted. One measurement is the same as plotted in Fig. 4. The other measurement was performed after the cleaning procedure described earlier. It is clearly visible that the nonequilibrium shape is artificially produced by the P-containing particles on the surface. After cleaning, an error function profile is obtained, which can be fitted by a constant diffusion coefficient. New experiments were performed involving the cleaning procedure described. In Fig. 7 five of the P–SIMS profiles obtained are plotted. Figure 7(a) shows two measurements after in-diffusion at different temperatures and times together with simulations fitted by a constant diffusion coefficient.

To investigate the arsenic vapor pressure dependence we annealed samples with different $p_{As^4}$. The profiles from experiments at 900 °C are plotted in Fig. 7(b). All three profiles show a good error function shape and clearly a positive pressure dependence. This means, P in-diffusion shows the same behavior as P interdiffusion described by Schultz et al. The shape of the profiles demonstrates that an equilibrium mechanism dominates the diffusion process. The positive arsenic pressure dependence indicates that P in-diffusion is governed by an interstitial-substitutional mechanism, too. Therefore, the possible diffusion mechanisms are the same as for P interdiffusion (Schultz et al.). The kick-out mechanism for P is given by

$$i_p = P_{As^4} + I_{As}$$

In Eq. (4), $i_p$ are P atoms on interstitial sites, $P_{As^4}$ are P atoms on As-lattice sites, and $I_{As}$, arsenic self-interstitials. In the limiting form that $i_p$ returns to a substitutional site after one diffusion step, this mechanism represents the usual interstitialcy mechanism. The Frank–Turnbull mechanism for the P diffusion is given by

$$i_p + V_{As} = P_{As^4}$$

The pressure dependence for these mechanisms is given by the following equation:
The pressure dependence, which can be calculated from the profiles in Fig. 7(b), is much higher than postulated by Eq. (6). We will discuss this behavior in detail later on.

B. Fermi-level effect during P in-diffusion

As mentioned earlier, we used differently doped samples to investigate the influence of charged point defects. Below 1000 °C, the doping level is much higher than the intrinsic carrier concentration. A possible Fermi-level effect on the arsenic sublattice should be measurable via the P in-diffusion at these samples. P is electrically isovalent if it is solved on an arsenic lattice site in GaAs. In the previous section, we have concluded that P in-diffusion is governed by an interstitial-substitutional mechanism. For the kick-out mechanism in Eq. (4), this means that charged \( i_P \) and charged \( i_A \) can influence the diffusion process. The Frank–Turnbull mechanism in Eq. (5) is determined by \( i_P \) and \( V_{As} \), which could be charged. Figure 8 shows three P in-diffusion profiles for differently doped samples, which were annealed under the same conditions. Similar experiments have been performed at 750, 850, and 950 °C. 

On the Ga sublattice, on the other hand, there is a clear indication that the native point defects can be charged, which influences the diffusion process strongly. The interdiffusion experiments on GaAs/AlAs heterostructures and impurity diffusion experiments evidence that negatively charged vacancies dominate the diffusion on the gallium sublattice in n-doped samples and positively charged gallium self-interstitials in p-doped samples.

C. Antimony in-diffusion in GaAs

Analogous to P in-diffusion experiments described earlier, we performed Sb in-diffusion experiments with pure Sb added to the ampoule. In Fig. 9, two Sb in-diffusion profiles for 1000 °C and different arsenic vapor pressures are plotted. The Sb in-diffusion shows the same behavior as does the P in-diffusion. The profiles can be fitted by error functions and the arsenic pressure dependence is positive, too. Between \( p_{As} = 0.18 \) bar and \( p_{As} = 10 \) bar the diffusion coefficient increases by a factor of 33. This is much higher than the value of 2.7 predicted by Eq. (6) and represent a behavior similar to that in Fig. 7 for P in-diffusion. We will discuss this problem in the following section.

For Sb in-diffusion we used a vapor pressure of \( p_{Sb} = 0.05 \) bar. The surface concentrations were much lower than for P in-diffusion experiments. We also studied the annealing at a higher Sb-vapor pressure (\( p_{Sb} = 2 \) bar), which, however, did not show an effect as high as that for P in-diffusion. This agrees with results of Bösker et al., who in their TEM investigations of Zn in-diffusion with additional Sb vapor observed a far smaller effect than if P vapor was added.

V. COMPARISON OF P AND SB IN- AND INTERDIFFUSION

P and Sb interdiffusion coefficients, presented already in Fig. 1, and recent P and Sb in-diffusion values without phase transformation are compared in Fig. 10. The recent values of P in-diffusion are now in the same range as P-interdiffusion values. P and Sb in-diffusion coefficients obtained under the
same experimental conditions (temperature, time, \( p_{\text{As}} \)) are nearly the same. For the in-diffusion of P and Sb this means, that the diffusion coefficient is independent of the species, like for the interdiffusion.

At higher temperatures, however, the in-diffusion coefficients are even smaller than the interdiffusion ones. One reason for this could be an evaporation from the surface during annealing. Bösker \(^5\) observed an evaporation from the GaAs surface at temperatures \( \geq 900 \, ^\circ \text{C} \) even in an arsenic atmosphere of \( p_{\text{As}} = 1 \) bar. They have investigated the arsenic self-diffusion via implanted \(^{76}\)As tracers. Due to the implantation a depth information is additionally available. Bösker \(^5\) found that a fitting of simulations to profiles after annealing is only possible if an evaporation in the nanometer range per hour is taken into account. They checked this assumption via weight measurements of the samples before and after annealing, revealing a significant mass reduction after annealing, which proved a possible evaporation of several nanometers. Mathematically, an evaporation can easily be taken into account by a transformation of the depth axis

\[
x' = x - v_c t.
\]

(7)

In Eq. (7), \( v_c \) is the evaporation rate, \( x' \), the new depth, and \( t \), the annealing time. If we use this transformation in Fick’s second law, we get the following equation, which describes the concentration profile in a diffusion process with a concurrent evaporation from the surface:

\[
\frac{\partial c(x', t)}{\partial t} = D \frac{\partial^2 c(x', t)}{\partial x'^2} + v_c \frac{\partial c(x', t)}{\partial x'}.
\]

(8)

At 1000 \( ^\circ \text{C} \), we performed two measurements for different times (20 and 72 h). If we simulate both times at a constant evaporation rate (7 nm/h) we can fit both profiles.\(^3\)\(^2\) The diffusion coefficient, which we need for this simulation, is higher than the values without considering evaporation (see corrected value in Fig. 10). This value is now comparable with the interdiffusion coefficients. To get more values we used experiments which were carried out with a high arsenic vapor pressure \( p_{\text{As}} = 10 \) bar, where the evaporation is reduced. This is the reason why the apparent pressure dependence of P and Sb in-diffusion (Figs. 7 and 9) is much stronger than can be concluded from Eq. (6). Due to the stronger evaporation at lower arsenic vapor pressures the calculated diffusion coefficients were too low. The interdiffusion data were obtained from experiments using an arsenic vapor pressure of 1 bar. To compare the in-diffusion data with the interdiffusion ones, we reduced the determined diffusion coefficients for \( p_{\text{As}} = 10 \) bar via Eq. (6) to a diffusion coefficient for 1 bar by dividing these values by a factor of 1.78. The other three corrected values of Fig. 10 have been evaluated in this way. These corrected values are of the same order of magnitude as the P and Sb interdiffusion values. From all the earlier values we obtain an Arrhenius expression for temperatures between 900 and 1100 \( ^\circ \text{C} \)

\[
D_{\text{As}}^{\text{SD}} = 75 \exp \left( \frac{4.4 \, \text{eV}}{kT} \right) \frac{\text{cm}^2}{\text{s}}.
\]

(9)

Below 900 \( ^\circ \text{C} \), the slope of the temperature dependence becomes lower. The present results do not allow us to decide unequivocally whether this behavior is a special feature of P in-diffusion or a general characteristic of As self-diffusion.

VI. DIFFUSION MODEL FOR ARSENIC SELF-DIFFUSION

In this section P and Sb diffusion coefficients are compared with earlier\(^1\)\(^5\)\(^6\) and more recent\(^5\) arsenic self-diffusion coefficients measured by radioactive tracers. As P and Sb in-diffusion values we use only the corrected ones as described earlier. Furthermore, we consider arsenic diffusion coefficients which were determined by sulfur in-diffusion and by nitrogen out-diffusion. The sulfur in-diffusion values had been calculated by Uematsu \(^5\),\(^1\) who fitted sulfur in-diffusion profiles of their own and profiles from the literature\(^3\)\(^4\)\(^5\) with simulation profiles. For the simulations they postulated only the kick-out mechanism, which explains all experimental data very well. Hence, these data represent that part of the arsenic self-diffusion involving arsenic self-interstitials \((D_{\text{As}} c_{\text{As}}^{\text{SD}}}/c_0)\). Analogously, the N out-diffusion measurements, which show also a nonequilibrium behavior, can be explained solely by the kick-out mechanism\(^6\) and allow to determine the As self-diffusion coefficients via As self-interstitials.

Figure 11 shows a compilation of diffusion coefficients based on all these different methods. Again, the good agreement (see Fig. 1) between P and Sb diffusion data and the arsenic self-diffusion ones is obvious. Hence, the recent data of both P and Sb in-diffusion and the As self-diffusion data support the assumption that P and Sb have tracer properties for arsenic diffusion in GaAs. The values obtained by impurity diffusion via the kick-out mechanism\(^1\)\(^5\)\(^6\) are only slightly lower than the As self-diffusion data. This supports the statement that As self-interstitials are the dominant native point defects in As self-diffusion. In a previous article\(^1\)\(^4\) we used
the N out-diffusion values cited in Ref. 5. Recently, these values have been corrected. In Fig. 11 the corrected values are shown.

For As self-diffusion we conclude from our investigations and the literature data that

$$D_{As}^{SD} = f_I D_{As}^I + f_V D_{As}^V \approx \frac{D_{f I} c_{eq}^I}{c_0},$$

(10)

where the geometrical factors $f_I$ and $f_V$ are assumed to be one in the case of GaAs. In contradiccion to the data of Palfrey et al. all new data lead to the conclusion that the As self-diffusion is governed by As self-interstitials. In Fig. 11 the solid line represents our result from Eq. (9) determined by P and Sb diffusion coefficients above 900 °C.

The dashed line is a fit from Bösker et al. which includes only the values determined by S and N diffusion. The activation energy of this line is 3.6 eV.

The dashed line in Fig. 11 represents a possible model which can explain the higher P diffusion data at lower temperatures (<900 °C). To explain the bending in the Arrhenius behavior, we suppose that for lower temperatures the Frank–Turnbull mechanism dominates the diffusion process of P diffusion (dashed line in Fig. 11). This means below 900 °C P diffusion does probably not represent the properties of the As self-diffusion.

VII. SUMMARY

We tried to explain the discrepancy between the former P in-diffusion data and P-interdiffusion ones. Due to a high P-vapor pressure there is a phase transformation on the GaAs surface to a polycrystalline GaAs$_{1-x}$P$_x$ phase, with a penetration depth much higher and not representing the diffusion coefficient of P in GaAs.

We have analyzed conditions where no extended defects are formed during the P in-diffusion. These experiments yielded error function profiles and a positive pressure dependence. Sb in-diffusion showed the same behavior. This allowed the conclusion that P and Sb in-diffusion are governed by interstitial-substitutional mechanisms in the same way as concluded by Schultz et al. for P and Sb interdiffusion.

The recent values of both P and Sb in-diffusion above 900 °C are even slightly lower than the interdiffusion ones. This can be explained by an evaporation of the surface during the diffusion. We obtain corrected diffusion coefficients by considering the evaporation in a simulation and by using high $p_{AS}$ where the evaporation is reduced. These diffusion coefficients are in good agreement with P and Sb interdiffusion data.

P and Sb diffusion data agree well with As self-diffusion data from radioactive tracer measurements. We conclude that P and Sb have tracer properties for arsenic and can be used to determine the self-diffusion on the arsenic sublattice in GaAs. Comparison of our data with literature data (Fig. 11) leads to the conclusion that the arsenic self-diffusion is determined by an activation energy between 3.6 and 4.4 eV.

Below 900 °C we have measured P in-diffusion coefficients which show a much weaker temperature dependence than above 900 °C. We postulate a model in which, at lower temperatures, the arsenic vacancies dominate P diffusion via the Frank–Turnbull mechanism whereas at higher temperatures, the arsenic self-interstitials dominate P diffusion via the kick-out mechanism or the interstitialcy mechanism as special case.

We also investigated the influence of charged point defects on the diffusion on the arsenic sublattice. P in-diffusion experiments on differently doped samples between 750° and 950 °C did not reveal any significant difference. Hence, there is no indication of a Fermi-level effect on the arsenic sublattice. Thus, we can conclude that the diffusion on the arsenic sublattice is governed by neutral point defects.

29. The measurements were performed by the company “RTG-Mikroanalyse” in Berlin, Germany.