Identification and Quantification of Defects in Highly Si-Doped GaAs by Positron Annihilation and Scanning Tunneling Microscopy

J. Gebauer,[1,*] R. Krause-Rehberg,[1] C. Domke,[2] Ph. Ebert,[2] and K. Urban[2]
[1]*FB Physik, Martin-Luther-Universität Halle, D-06099 Halle, Germany*
[2]*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*
(Received 2 December 1996)

Defects in highly Si-doped GaAs were identified and their concentration determined by combining positron lifetime spectroscopy with scanning tunneling microscopy. We observed with increasing Si-doping concentration an increasing concentration of a deep positron trap identified as Si_{Ga}-donor–Ga-vacancy complex. The concentration of shallow positron traps increased with the Si concentration too. The shallow traps are found to be Si_{As} acceptors and Si clusters. [S0031-9007(97)03056-1]

PACS numbers: 61.72.Ji, 61.16.Ch, 78.70.Bj

Although it has been long known that point defects govern key properties of semiconductors, it remains difficult to determine reliably the nature and concentration of the defects. Current techniques mostly measure signals of many defects simultaneously, thus rendering an interpretation difficult. A combination of two different methods, each separately insufficient to provide detailed information about the defects present, can solve this problem. In this Letter we combine positron lifetime spectroscopy (POLIS) with scanning tunneling microscopy (STM) and take advantage of the strengths of both methods: STM will be used to provide a direct image and identification of the defects, while POLIS will probe the concentrations of the bulk defects. We can thus compensate on the one hand the insufficiencies of POLIS that it is in general not possible to relate unambiguously the observed positron signal to the exact nature of the defect which trapped the positron [1–4], i.e., different defects may lead to the same positron lifetime and therefore may not be recognized as separate defect species. On the other hand, we avoid that the formation of additional defects (such as vacancies) on the surface after cleavage obscures the exact measurement by STM of the concentration of, e.g., bulk vacancies exposed on the surface [5].

We illustrate the methodology of the combined analysis on compensating defects in highly Si-doped GaAs. We show that the positron annihilation signatures attributed to vacancies arise from Si_{Ga}-donor–Ga-vacancy complexes and not from As vacancies or other defects as suggested previously, whereas the signal associated with shallow positron traps arises from Si_{As} acceptors and Si clusters. We demonstrate that STM combined with positron annihilation provides an unambiguous determination of the compensating defects and their concentration present in crystals.

We investigated seed-grown GaAs crystals with Si concentrations of 1×10^{18}, 2.7×10^{18}, 1.2×10^{19} and $(2.5–6) \times 10^{19}$ cm^{-3}. The carrier concentrations of 0.7×10^{18}, 1×10^{18}, 4.5×10^{18}, and 1.8×10^{18} cm^{-3} at 100 K, respectively, indicate a high compensation. The positron lifetime spectroscopy was performed with a conventional fast-fast coincidence system (time resolution 250 ps) in a temperature range of 20 to 500 K. A ^{22}NaCl positron source (activity 8×10^5 Bq, covered with 1.5 μm Al foil) was placed between a pair of identical samples [4]. The spectra were analyzed with the trapping model after source and background correction. The same wafers were also cleaved in ultrahigh vacuum to form clean (110) surfaces and investigated by STM. The exposed bulk defects were identified and their concentrations determined.

First, positron lifetime spectra were measured at room temperature. The average positron lifetime τ_{av} increases with increasing Si concentration from 238 to 259 ps (Fig. 1). All measured average positron lifetimes are well above the positron lifetime in GaAs (τ_b) determined to be (228.5 ± 1) ps in reference samples showing no positron trapping. This value is in good agreement with previous results [1,4] and theoretical expectations [6]. These observations suggest an increasing concentration

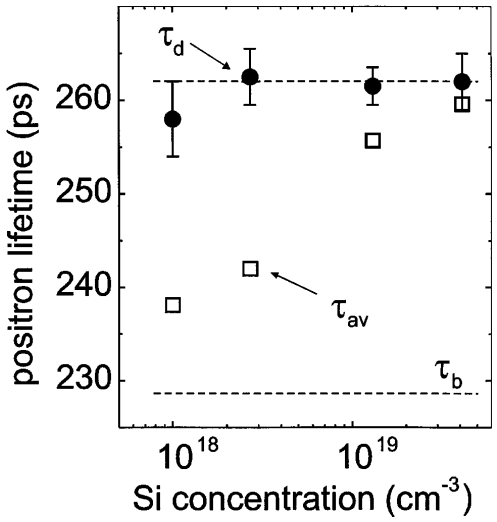

FIG. 1. Average positron lifetime τ_{av} and defect related lifetime τ_d as a function of the Si concentration (measured by SIMS) in Si-doped GaAs at room temperature. τ_b is the positron lifetime in defect-free GaAs.

 0031-9007/97/78(17)/3334(4)$10.00

of vacancy defects with increasing Si concentration. We analyzed the data using a two-state trapping model assuming positron annihilation in the bulk and in one defect. We obtained a positron lifetime τ_d in the defect of (262 ± 2) ps. An analysis with more trapping states did not reveal additional lifetime components. A positron lifetime of about 260 ps in GaAs is commonly attributed to annihilation in monovacancies [6–8]. However, it is not clear whether these vacancies are isolated As vacancies [1], isolated Ga vacancies [3], defect complexes consisting of either a Ga or As vacancy and other defects [4], or any combination of the mentioned defects. For a detailed identification of the vacancy defect(s) we need the STM measurements discussed below.

The average positron lifetime τ_{av} decreases with decreasing temperature between 100 to 300 K (Fig. 2). At low and at high temperatures nearly constant values are reached. The average positron lifetime at high temperatures is close to the room temperature values discussed above. The low temperature ($T < 80$ K) values are closer to the positron lifetime in defect-free GaAs. The change of the lifetime cannot be due to a change of the charge of the vacancies, because in our degenerately doped samples the Fermi level remains in the conduction band at low temperatures [1,3]. Thus at low temperatures additional positron trapping centers act with a positron lifetime close to that of the bulk GaAs. This indicates that the additional traps have no open volume. Such defects are commonly known as shallow positron traps [9], which cannot be detected at higher temperatures due to a thermal detrapping of the positrons. Shallow positron traps are mostly attributed to negatively charged ions [6,8,9]. However, we cannot determine the exact nature of the shallow traps from the positron annihilation data alone.

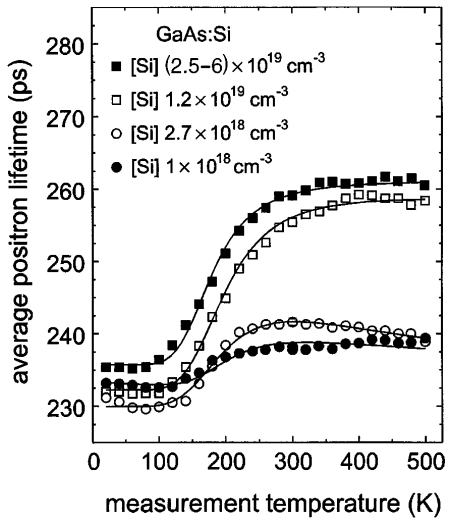

FIG. 2. Average positron lifetime τ_{av} as a function of the temperature for different Si doping levels. Solid lines are fits to the experimental data with the assumption of positron trapping at negatively charged vacancies and negative ions.

At this stage we determine the concentration of the vacancy defects. Since the influence of the shallow traps is negligible at high temperatures, we analyze that part of the data with the two-state trapping model as used above. The concentration of the vacancy defects c_v can be determined using the relation $c_v = \kappa_v/\mu_v$, with μ_v being the trapping coefficient and κ_v being the trapping rate of the positrons in the vacancies. The trapping rate has been calculated according to $\kappa_v = \tau_b^{-1}(\tau_{\mathrm{av}} - \tau_b)/(\tau_d - \tau_{\mathrm{av}})$ [1,4]. For negatively charged monovacancies the trapping coefficient is 10^{15} s^{-1} at room temperature [10]. The vacancies are negatively charged, because if they were uncharged (temperature independent trapping coefficient), the presence of the negatively charged shallow traps would induce a continuous decrease of the positron lifetime with decreasing temperature until the positron lifetime of the shallow traps is reached. This is not observed (plateaus at different levels from 20 to 80 K in Fig. 2). Hence the trapping coefficient of the vacancies must have the same temperature dependence as that one of the shallow positron traps (proportional to $T^{-1/2}$ [6]. Consequently, the vacancy has the same sign of charge as the shallow trap, which has been identified to be a negatively charged ion. Uncharged or positively charged ions would not trap positrons. Thus the vacancy defect is negatively charged [6]. This result is consistent with theoretical expectations for vacancies in highly n-doped GaAs [11]. Figure 3(a) shows that the vacancy concentration increases with the Si concentration. The vacancy

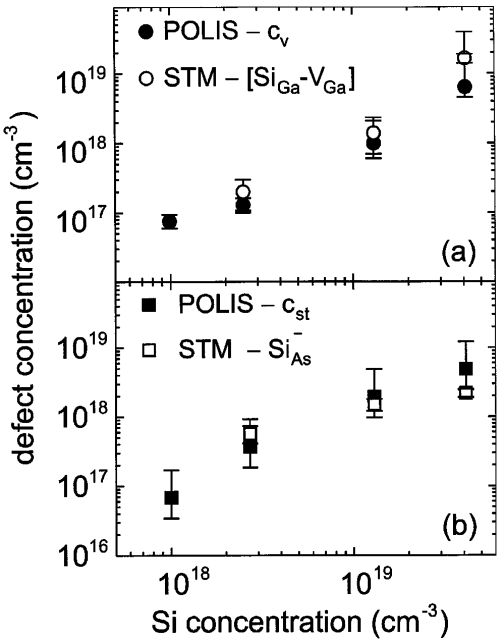

FIG. 3. (a) Concentrations of monovacancies from POLIS (filled circles) and Si_{Ga}-V_{Ga} complexes determined from STM images (open circles) as a function of the Si concentration. (b) The same for shallow positron traps (filled squares) and Si_{As} acceptors observed in STM images (open squares).

concentration for the highest doped sample is a lower-limit estimation due to saturated positron trapping, i.e., the average lifetime is close to τ_d.

The next step is the determination of the concentration c_{st} of the shallow positron traps. Only at very low temperatures the positron detrapping from the shallow traps can be neglected. We determine their concentration from the data at 20 K using a three-state trapping model, which assumes annihilation in vacancy defects, at negative ions, and in the bulk. In order to determine the trapping rate in the shallow traps $\kappa_{st} = c_{st}\mu_i$ we first separate the trapping rate of the vacancy defects ($\kappa_v = c_v\mu_v$) at 20 K. Using the temperature dependence of the trapping coefficient [6,12] we calculated a value of $\mu_v = 1.5 \times 10^{16}$ s^{-1} at 20 K, in good agreement with Ref. [2]. Now we can deduce the trapping rate in the shallow traps and their concentration c_{st}, if we know the trapping coefficient μ_i of the ions. The latter was taken to be $(5 \pm 2) \times 10^{16}$ s^{-1} at 20 K [8]. Figure 3(b) shows that the concentration of the shallow traps increases over two orders of magnitude with increasing Si concentration. We should note that the large error bars arise mostly due to uncertainties of the temperature dependence of the trapping coefficients, which cannot be measured separately and must be determined by fitting procedures to similar positron lifetime data [8,12]. Finally, we checked the model assumptions by fitting τ_{av} as a function of sample temperature using only the binding energy between positrons and shallow traps as fitting parameter (c_v and c_{st} fixed). A good agreement is obtained (solid lines in Fig. 2) showing that the analysis is consistent. Uncharged vacancies did not provide any acceptable agreement with the data. The binding energy (lowest energy level which can be reached by positrons [6,12]) is found to be (70 ± 15) meV. The value agrees well with that found for Ga antisites in electron irradiated GaAs [(50 ± 10) meV] [8] and with the calculated lowest energy state in the Rydberg potential of a single negatively charged ion (82 meV) [12].

In order to identify the nature of the positron trapping centers we performed STM investigations of the defects exposed by cleavage on nonpolar (110) surfaces, which are well suited for the identification of point defects [13,14] due to their simple 1×1 reconstruction and the absence of surface states in the fundamental band gap. In more than 900 STM images (20×20 nm^2) we classified all defects observed according to their properties (charge, localized features, etc.), time dependencies, and concentrations. We observed five defects having significant concentrations (other defects had concentrations below the sensitivity limit of about 2×10^{17} cm^{-3}). The five defects were identified as Si_{Ga} donor, Si_{As} acceptor, Si cluster, Ga monovacancy, and Si_{Ga}-donor–Ga-vacancy complex [5]. The Si_{Ga} donor does not trap positrons and thus it is not relevant in the following discussion. The two vacancy defects are candidates to be the deep positron trap(s) and the two remaining defects (Si acceptors and Si clusters) are candidates for the shallow positron traps. First we focus on the deep positron traps.

The Ga vacancies are formed after cleavage on the surface similar to previous observations on InP(110) and GaAs(110) surfaces [15]. This low-temperature Langmuir desorption is driven by the Fermi-level effect: Cation (anion) vacancies are formed to compensate the n-type (p-type) doping atoms [16]. Thus the observed concentrations do not reflect the bulk concentrations of Ga vacancies. In order to determine the bulk concentration an extrapolation to the cleavage time has been applied [5]. Within the error margins of the extrapolation we could not detect isolated Ga vacancies at cleavage time. Thus the Ga vacancies are surface related and cannot be the origin of the positron trapping at vacancies in the bulk.

Figures 4(a) and 4(b) show high-resolution STM images of the occupied and empty states of the second vacancy defect. The concentration of this defect increases with increasing Ga vacancy and Si concentration. These characteristics suggest that the defect consists of a Si dopant atom and a Ga vacancy. The result is corroborated by an analysis of the STM images: One empty dangling

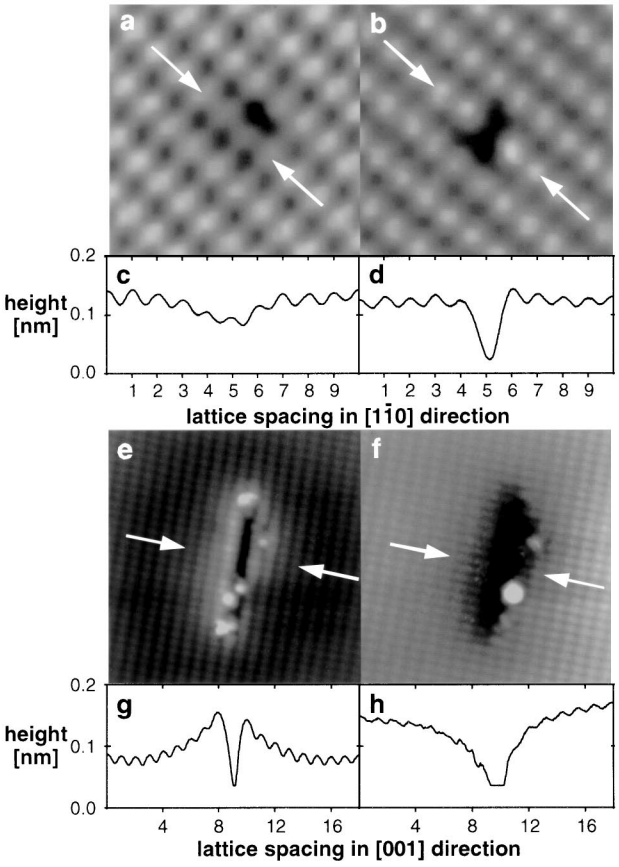

FIG. 4. Constant-current images of the occupied (a) and empty states (b) of a Si_{Ga}-V_{Ga} complex. (c) and (d): Line profiles along the atomic rows marked with the arrows in frames (a) and (b), respectively. (e) to (h): The same displays for a Si cluster.

bond is missing and one empty neighboring dangling bond appears raised [Figs. 4(c) and 4(d)]. An analogous structure was observed for Zn_{Ga}−anion-vacancy complexes on *p*-doped GaAs and InP(110) [16]. Only the sublattice of the vacancy and the charge states are interchanged. The vacancy gives rise to the missing empty dangling bond feature, whereas the raised neighboring dangling bond is the signature of the Si atom. Because the complex is uncharged on the surface (no band bending observed), the Si atom and the surface vacancy have the same magnitude of charge with opposite sign. Since the isolated Ga vacancy is negatively charged, the Si atom must be positively charged. This is the charge state of the Si_{Ga} donor. Thus Fig. 4 shows a Si_{Ga}-donor−Ga-vacancy complex. In the bulk the complex is known to be negatively charged [17]. On the surface the charge-transition levels are shifted compared to the bulk. We calculated from the measured surface concentrations the bulk concentrations, assuming that uncharged defects are observed only in the top layer [5] [open circles in Fig. 3(a)]. A good agreement between the concentrations of the deep positron traps and the Si_{Ga}-donor−Ga-vacancy complex is obtained. Thus the monovacancies probed by POLIS are Si_{Ga}-donor−Ga-vacancy complexes in agreement with calculations [17], but in contrast to As vacancies observed in low and undoped *n*-type GaAs [1]. We did not observe As vacancies in as grown highly Si-doped GaAs by STM.

At this stage we discuss the nature of the shallow positron traps. The only negatively charged ion observed by STM is the Si_{As} acceptor. The concentration of these acceptors can be obtained reliably from STM images, because dopants can be observed up to six layers below the surface [14]. We measured the concentration for each subsurface layer and calculated the bulk concentration [open squares in Fig. 3(b)]. A good agreement is reached with the POLIS results for the lower-doped samples. A significant deviation is observed only for the highest doped sample. We suggest that the deviation is due to trapping of positrons in Si clusters, which are present at very high Si concentration [5]. The Si clusters can trap positrons, because the band offsets at the closed Si-GaAs interface (the Si is an enclosed precipitate) induce a local potential raise. This is equivalent to a local upward band bending (downward attractive potential for the positron) [Fig. 4(e) to 4(h)], which has the same features in STM images as the screened Coulomb potential around negatively charged Si acceptors. A similar effect was observed around GaN clusters in GaAs(110) [18]. The image features of Si clusters and GaN clusters are identical. Thus the precipitates may also trap positrons. Such a trapping does not yield an additional positron lifetime component, because the positron lifetime in Si is only about 10−12 ps lower than GaAs [6,19]. This close component cannot be resolved. Therefore, two physically different defects may act as shallow positron traps at very high doping concentrations.

In summary, we demonstrated that the combined analysis of positron lifetime spectroscopy (POLIS) and scanning tunneling microscopy is a powerful tool to identify the nature of defects and to determine their concentrations in highly Si-doped GaAs. The vacancies probed by POLIS are Si_{Ga}-donor−Ga-vacancy complexes. Their concentration increases with increasing Si concentration. No As vacancies were found. Si_{As} acceptors and Si clusters act as shallow traps and their concentration increases with the Si concentration too. Analogous combinations of two complementary methods (such as positron annihilation and scanning tunneling microscopy presented here) may serve as the basis for testing present theoretical concepts of point defects and thus initiate significant advances in the atomic-scale understanding of the macroscopic properties of electronic materials.

The authors thank S. Eichler and A. Polity for discussions and K. H. Graf for technical support.

Note added.—After the initial submission of this paper another positron annihilation study concluded that Ga vacancy related defects exist in highly Si-doped molecular-beam epitaxy grown GaAs layers [20], corroborating our results.

*Electronic address: e3ebq@mlucom.urz.uni-halle.de

[1] K. Saarinen *et al.*, Phys. Rev. B **44**, 10 585 (1991).
[2] K. Saarinen *et al.*, Phys. Rev. Lett. **70**, 2794 (1993).
[3] S. Chichibu *et al.*, J. Appl. Phys. **73**, 3880 (1993).
[4] R. Krause-Rehberg *et al.*, Phys. Rev. B **49**, 2385 (1994).
[5] C. Domke *et al.*, Phys. Rev. B **54**, 10 288 (1996).
[6] M. J. Puska and R. M. Nieminen, Rev. Mod. Phys. **66**, 841 (1994).
[7] L Gilgien *et al.*, Phys. Rev. Lett. **72**, 3214 (1994).
[8] K. Saarinen *et al.*, Phys. Rev. B **52**, 10 932 (1995).
[9] K. Saarinen *et al.*, Phys. Rev. B **39**, 5287 (1989).
[10] R. Krause-Rehberg and H. S. Leipner, Appl. Phys. A (to be published).
[11] See, e.g., M. J. Puska, J. Phys. **1**, 7347 (1989); R. W. Jansen and O. F. Sankey, ibid. **39**, 3192 (1989); S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991); T. Y. Tan, H.-M. You, and U. M. Gösele, Appl. Phys. A **56**, 249 (1993).
[12] C. Corbel *et al.*, Phys. Rev. B **45**, 3386 (1992).
[13] G. Lengel *et al.*, Phys. Rev. Lett. **72**, 836 (1994); Ph. Ebert, K. Urban, and M. G. Lagally, ibid. **72**, 840 (1994).
[14] M. B. Johnson *et al.*, Appl. Phys. Lett. **63**, 3636 (1993); R. M. Feenstra, J. M. Woodall, and G. Pettit, Phys. Rev. Lett. **71**, 1176 (1993); J. F. Zheng *et al.*, ibid. **72**, 1490 (1994).
[15] Ph. Ebert *et al.*, Phys. Rev. B **51**, 9696 (1995).
[16] Ph. Ebert *et al.*, Phys. Rev. B **53**, 4580 (1996); J. Vac. Sci. Technol. A **14**, 1807 (1996).
[17] J. E. Northrup and S. B. Zhang, Phys. Rev. B **47**, 6791 (1993).
[18] R. S. Goldman *et al.*, Appl. Phys. Lett. **69**, 3698 (1996).
[19] S. Dannefaer, Radiat. Eff. Defects Solids **111–112**, 65 (1989).
[20] T. Laine *et al.*, Phys. Rev. B **54**, 11 050 (1996).