PHYSICAL REVIEW B **67**, 235207 (2003)

Determination of the Gibbs free energy of formation of Ga vacancies in GaAs by positron annihilation

J. Gebauer,[1,2,*] M. Lausmann,[1] F. Redmann,[1] R. Krause-Rehberg,[1] H. S. Leipner,[3] E. R. Weber,[2] and Ph. Ebert[4]
[1]*Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany*
[2]*Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, California 94720, USA*
[3]*Interdisziplinäres Zentrum für Materialwissenschaften, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany*
[4]*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*

(Received 14 January 2003; published 27 June 2003)

We determined the Gibbs free energy of formation—i.e., the formation enthalpy and entropy—as well as the charge state of Ga vacancies in *n*-type GaAs by directly probing the vacancy concentration as a function of annealing temperature, arsenic vapor pressure, and doping concentration using positron annihilation. The Ga vacancy concentration increases with doping concentration and arsenic vapor pressure, but decreases with temperature. Using equilibrium thermodynamics, we obtained a $-3e$ charge state of the Ga vacancy in *n*-doped GaAs as well as a formation enthalpy of (3.2 ± 0.5) eV and a formation entropy of $(9.6\pm1)k_B$ for the uncharged vacancy state.

DOI: 10.1103/PhysRevB.67.235207 PACS number(s): 61.72.Ji, 61.72.Bb, 78.70.Bj

I. INTRODUCTION

Point defects govern to a large degree the properties of semiconductors by introducing localized electronic states in the band gap, which were the focus of intense research over the years. However, the degree to which point defects can affect semiconductors depends primarily on the defect concentration. In thermal equilibrium the concentration is determined by the Gibbs free energy of formation (G_f) of the defect: i.e., the sum of the formation enthalpy (H_f) and formation entropy (S_f) multiplied by the temperature ($G_f = H_f - T\,S_f$). Thus, for a quantitative understanding and eventual prediction of the macroscopic properties of the semiconductor, it is crucial to determine the thermodynamic quantities governing the concentration of defects, in addition to the electronic properties of the defect.

Unfortunately, the determination of the Gibbs free energy of formation of defects in semiconductors turned out to be rather difficult as shown exemplarily for one of the most investigated cases, the Ga vacancy in GaAs: On the experimental side, mostly diffusion experiments have been used to extract the enthalpy and entropy of formation.[1,2] However, these experiments do not probe directly the vacancies, but rather the diffusion mediated by vacancies, making the analysis very sensitive to the diffusion model used. Indeed, large deviations result (e.g., 2 vs 4 eV for the formation enthalpy[1,2]). On the theoretical side, with exception of Ref. 3, only formation enthalpies have been addressed, thus neglecting the contribution of the entropy. Moreover, theoretical[3] and experimental results[1] deviate significantly. In addition, the electronic properties of the defect—namely, its charge state—contribute significantly to the Gibbs free energy of formation.[4] This is especially critical considering the still debated charge state of the Ga vacancy in *n*-type GaAs. Calculations predict a charge of $-3e$ (Refs. 5–7), while recent diffusion experiments suggest a charge of $-2e$ (Ref. 2) or $-1e$ (Ref. 8) (e is the elementary charge). In view of this situation, a determination of the enthalpy and entropy of formation *and* the corresponding charge state of the Ga vacancy is needed.

In this work, we determine the Gibbs free energy of formation and the charge state of the Ga vacancy in GaAs by directly probing the vacancy concentration with positron annihilation (PA) as a function of doping concentration, temperature, and chemical potential (or stoichiometry).

In order to avoid the difficulties of previous measurements probing the formation of vacancies in semiconductors, we modified the methodology in a few but significant points: (i) Positron annihilation allows us to identify simultaneously the concentration and the type of the vacancies present,[9] unlike diffusion experiments where the defects are not directly probed. (ii) By using a modified annealing procedure, we avoid PA measurements at high temperatures, which yielded divergent results for other semiconductors.[10,11] In our experiments we generate the equilibrium concentration of Ga vacancies by annealing the GaAs samples in a two-zone furnace, which allows us to separately control the thermodynamic variables arsenic vapor pressure (p_{As}) and sample temperature. According to the Gibbs phase rule, this establishes a defined equilibrium concentration of defects in the compound GaAs.[12,13] The control of only one variable—e.g., temperature—would not result in a defined thermodynamic equilibrium. The vacancy concentration is preserved through quenching, which allows us to perform PA measurements at low temperatures. (iii) We choose primarily Te-doped GaAs for our investigations, because Te is only incorporated on the As sublattice.[14,15] Therefore, annealing of Te-doped GaAs results only in Ga vacancies (V_{Ga}) and Ga-vacancy–Te-dopant (V_{Ga}-$\mathrm{Te}_{\mathrm{As}}$) complexes without the formation of additional dopant-related defects as in, e.g., Si-doped GaAs.[16,17]

Preliminary investigations have shown that the experimental procedure yields a defined equilibrium concentration of vacancies in GaAs:Te, demonstrating the validity of our approach.[18,19] In the present work, we extend and complete the investigation of vacancies in Te-doped GaAs. The analysis of the data by means of equilibrium thermodynamics[12,20] then allows us to determine the Gibbs free energy of formation of Ga vacancies.

The paper is organized as follows: Section II describes the experimental details. Section III deals with the identification and quantification of the Ga vacancies in GaAs:Te as the foundation of the further investigations and with the dependence of the vacancy concentration on annealing time, As vapor pressure, and doping. It is shown that the annealing results in the equilibrium concentration of Ga vacancies. The results are analyzed in Sec. IV where we determine the Gibbs free energy of formation of Ga vacancies.

II. EXPERIMENT

We investigated melt-grown, *n*-doped GaAs bulk crystals having Te concentrations from 1.1×10^{16} to 6×10^{18} cm^{-3}. The dopant concentration was determined by secondary-ion mass spectroscopy (SIMS) and the carrier concentration by Hall effect measurements at room temperature in selected samples.

In order to obtain the equilibrium concentration of vacancies, the samples were annealed together with metallic arsenic in evacuated quartz-glass ampoules in a two-zone furnace.[18,19] The two-zone furnace allowed us to independently control the sample temperature and As vapor pressure p_{As}, which is determined by the temperature of the metallic As source, but independent of the sample temperature.[21] After annealing, the samples were fast quenched (cooling rate 60 K/s) to room temperature, where Ga vacancies form stable complexes with donors.[22,23] We found that slower quenching with a cooling rate down to 10 K/min had no influence on the resulting vacancy concentration. Prior to the measurements, a layer of $\sim$30 μm was etched from each sample surface in order to measure exclusively bulk effects.

The vacancy concentration was determined by positron lifetime spectroscopy using a conventional fast-fast coincidence system with a time resolution [full width at half maximum (FWHM)] of $\sim$250 ps. Measurements were performed at temperatures between 20 and 600 K. The positron lifetime spectra were analyzed with the trapping model after source and background corrections.[9] Here 2×10^{6}–5×10^{6} events were collected in each lifetime spectrum.

A positron lifetime spectrum consists of a sum of exponential decay terms, characterized by their intensities I_i and lifetimes τ_i. A simple and statistically robust way to characterize the spectrum is the average positron lifetime $\tau_{\mathrm{av}}=\Sigma I_i\tau_i$ with $\Sigma I_i=1$. In a defect-free sample, positrons annihilate with a characteristic single lifetime τ_{bulk} [229 ps at 300 K in GaAs (Ref. 24)], which corresponds to τ_{av} in that case. If positrons are trapped in vacancies, a second defect specific lifetime τ_v, always longer than τ_{bulk}, is present.

From the positron lifetime measurement, the trapping rate κ_v of positrons into vacancies can be obtained by

$$\kappa_v=\frac{1}{\tau_{\mathrm{bulk}}}\frac{(\tau_{\mathrm{av}}-\tau_{\mathrm{bulk}})}{(\tau_v-\tau_{\mathrm{av}})}=\mu_v c_v\,. \tag{1}$$

Here κ_v is related to the vacancy concentration c_v via the trapping coefficient μ_v. The trapping coefficient must be determined with an independent reference method. This will be shown for V_{Ga}-$\mathrm{Te}_{\mathrm{As}}$ complexes in Sec. III B.

The positron lifetime depends mainly on the electron density at the annihilation site and provides thus information on the open volume of a defect. Further information can be obtained by studying the electron-positron annihilation momentum distribution. At high momentum, the momentum distribution is dominated by annihilation with core electrons. Shape and intensity of the momentum distribution can therefore be used to study the chemical surrounding of defects.[25] We observed the annihilation momentum distribution by coincidence spectroscopy using a setup of two Ge detectors.[26] The intensity of the core annihilation was quantified by the line shape parameter W, defined as the intensity in the momentum range $(15–20)\times10^{-3}m_0c$ with m_0 being the rest mass of the electron and positron and c the speed of light. Measured W parameters are normalized to the value $W=0.0074$ of a Zn-doped GaAs reference free from positron trapping at vacancies.[24] In combination with positron lifetime spectroscopy, the measurements of the momentum distribution allow us the identification of the vacancies observed.[23,25]

III. DEFECTS IN ANNEALED GaAs:Te

A. Identification of Ga vacancies

As the base of our investigations, it is necessary to identify and quantify the vacancies with positron annihilation. We start with the identification of Ga-vacancy–Te-donor complexes by a combination of positron lifetime spectroscopy and measurements of the annihilation momentum distribution.

In Fig. 1, the average [frame (b)] and defect-related [frame (a)] positron lifetime is shown as a function of the measurement temperature, as it is typically found in annealed GaAs:Te. The different As vapor pressures (0.2 and 5.6 atm) represent the range of pressures used in our experiments. All samples have a τ_{av} above that in bulk GaAs determined in a GaAs:Zn reference. This shows clearly the presence of vacancy defects.

A temperature dependence of τ_{av} in GaAs:Te as observed in Fig. 1 indicates that positrons are trapped at negatively charged vacancies and acceptor-type ions.[9] The ions trap positrons only at low temperature and have a positron lifetime close to τ_{bulk} (Ref. 27). With increasing temperature, a larger fraction of positrons annihilates in vacancies, causing the increase in τ_{av} between 100 and 200 K. The decrease in τ_{av} at $T>200$ K indicates positron trapping at negative vacancies: trapping at neutral vacancies would be independent of temperature.[28] The solid lines in Fig. 1 are obtained from a fit to the data considering competing positron trapping and detrapping from negative ions and vacancies as described earlier.[23,29] We obtained a binding energy of (65 ± 20) meV of positrons to the shallow potential caused by the negatively charged ions, in agreement with previous results.[23,29,30] Acceptor-type ions detected by PA are attributed to intrinsic defects (e.g., $\mathrm{Ga_{As}}^{2-}$) (Refs. 27 and 29) or

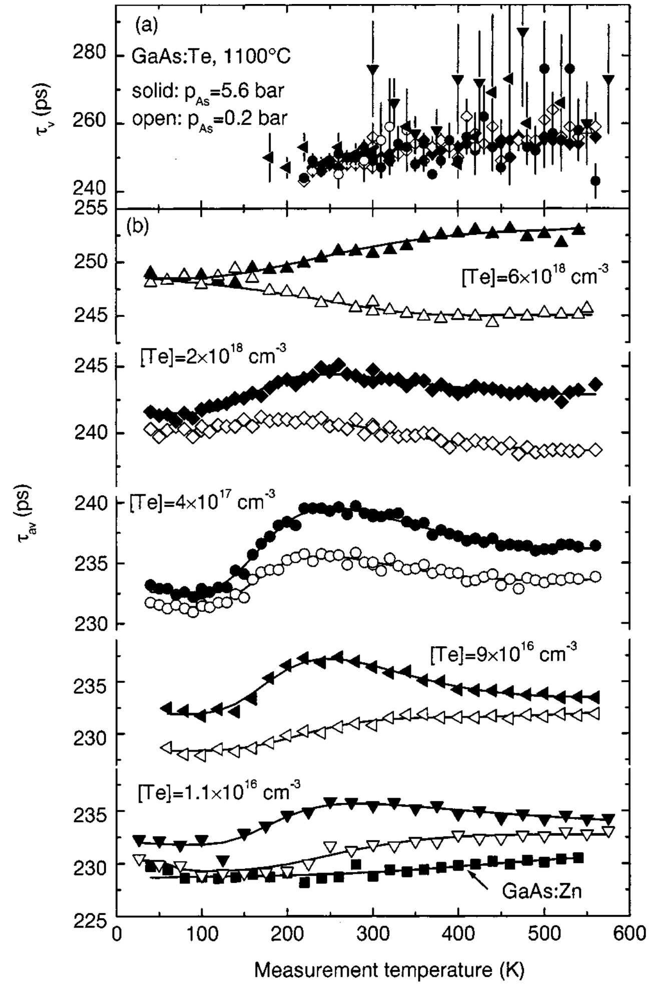

FIG. 1. Defect-related positron lifetime τ_v (a) and average positron lifetime τ_{av} (b) vs the measurement temperature in GaAs:Te with different Te concentrations, annealed for 24 h at 1100 °C at an As vapor pressure p_{As} of 5.6 atm (solid symbols) or 0.2 atm (open symbols) in comparison to a GaAs:Zn reference (solid squares).

extrinsic impurities.[30] However, PA alone does not allow their identification.[9,27] The nature of the ions will be discussed in Sec. III D.

The decomposition of the positron lifetime spectra yields a defect-related positron lifetime τ_v of (254±5) ps at room temperature. This value is typical for monovacancies in GaAs. In fact, it is the same positron lifetime as found earlier for Ga-vacancy–Te-donor complexes.[23] Thus we attribute the vacancies in annealed GaAs:Te also to V_{Ga}-Te_{As}. Evidently, the average positron lifetime—i.e., the vacancy concentration [Eq. (1)]—depends on the doping concentration, but is also influenced by the As vapor pressure. These effects will be analyzed in detail below.

In order to confirm the assignment above, we use additional information from the annihilation momentum distribution. Positron annihilation characteristics are the superposition of contributions from the different annihilation sites. The average positron lifetime depends therefore linearly on the *W* parameter as long as only the vacancy concentration varies and the defect type is the same.[23,31] In Fig. 2, the *W* parameter is shown as a function of the average positron lifetime for all GaAs:Te samples investigated. Different data points for a given doping concentration correspond to different annealing conditions: i.e., As vapor pressures and/or annealing temperatures. τ_{av} depends linearly on the *W* parameter, showing that the same defect type is present in all GaAs:Te samples independent of the annealing procedure. The linear fit contains also the annihilation parameter determined earlier for V_{Ga}-Te_{As} ($W=0.76$, $\tau=254$ ps, Ref. 23). Therefore, the vacancy defects in annealed GaAs:Te are also V_{Ga}-Te_{As} complexes, regardless of the particular dopant concentration and thermal treatment.

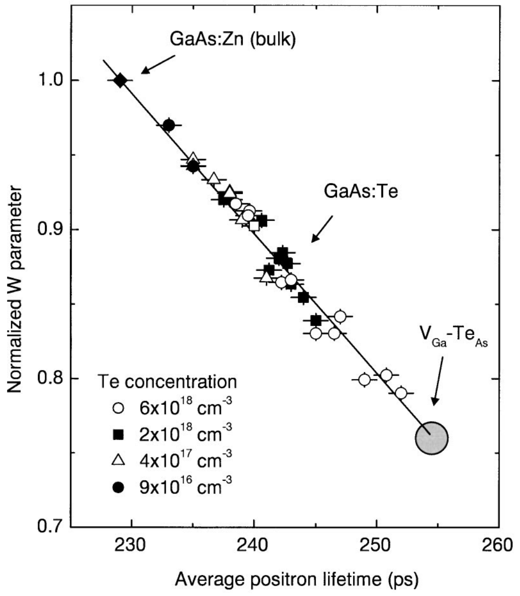

FIG. 2. Average positron lifetime as a function of the *W* parameter of the electron-positron annihilation momentum distribution for differently high-Te-doped GaAs. The *W* parameter is normalized to the value found in GaAs:Zn. All samples were annealed at 1100 °C: different data points for a given Te concentration correspond to different As vapor pressures or annealing temperatures. The solid line is a linear fit to the data, showing that all samples contain the same defect type. The defect is identified to be a V_{Ga}-Te_{As} complex; the annihilation parameters are indicated by the gray circle (see text).

B. Trapping coefficient of V_{Ga}-Te_{As}

On the basis of the identification above we can now discuss the quantification of the vacancies. The vacancy concentration c_v can be obtained from the positron trapping rate κ_v at 550 K with Eq. (1). The data at 550 K are used because only vacancies, but no defects without open volume—i.e., acceptor-type ions—trap positrons at higher temperature.[9,27] The determination of absolute vacancy concentrations requires exact knowledge of the trapping coefficient μ_v in Eq. (1). Therefore, we determined the trapping coefficient by quantifying the electrical compensation through V_{Ga}-Te_{As} complexes in samples having a low concentration of acceptor-type ions: i.e., where the compensation is dominated by the vacancies. Then the concentration of compensated carriers ($n_{comp}=[Te]-n_e$) is given by (n_{comp}

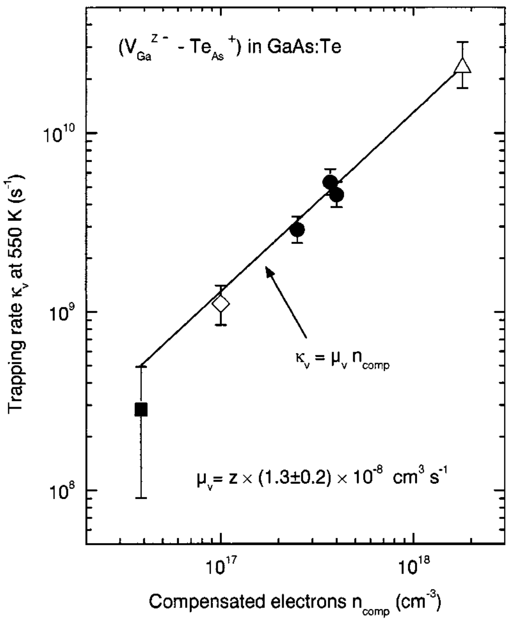

FIG. 3. Positron trapping rate into V_{Ga}-Te_{As} at 550 K as a function of the concentration of compensating acceptors. The solid line is a linear fit to the data to determine the positron trapping coefficient μ_v (see text). The data are from GaAs doped with 9×10^{16} (■), 4×10^{17} (◇), 2×10^{18} (●), and 6×10^{18} (△) cm^{-3} Te, respectively. We obtain the trapping coefficient $\mu_v = z\times(1.3\pm0.2)\times10^{-8}$ cm^3 s^{-1} where z is the charge state of the isolated Ga vacancy.

$=z\,[V_{Ga}$-$Te_{As}])$ where [Te] is the Te concentration determined by SIMS and n_e is the carrier concentration determined by Hall effect measurements. z is the charge (in units of e) of the *isolated* Ga vacancy because each $V_{Ga}{}^{z-}$ compensates z singly positively charged $Te_{As}{}^{+}$ donors when assuming that the charge of the complex is the sum of the charges of the single defects.[15,32]

In Fig. 3, the positron trapping rate κ_v is shown as a function of the concentration of compensated carriers. The solid line is a linear fit with $(\kappa_v = n_{comp}\mu_v)$ involving the above assumption that the compensation is caused exclusively by Ga vacancy donor complexes. The linear dependence between trapping rate and concentration of compensated carriers strongly supports this assumption. From the fit, we obtained $\mu_v = z\times(1.3\pm0.2)\times10^{-8}$ cm^3 s^{-1} [equivalent to $\mu_v^{at} = z\times(5.8\pm1.0)\times10^{14}$ s^{-1} in atomic units]. In the following, we use $\mu_v^{at} = 1.74\times10^{15}$ s^{-1} corresponding to $z=3$, although the vacancy charge is not known at this stage. Its determination will be described below. Our value of μ_v is in good accordance with previous results, but is more accurate.[9] On this basis we are now able to determine the vacancy concentrations of all samples subjected to different annealing conditions.

C. Equilibrium concentration of V_{Ga}

In this section, we show that the annealing procedure indeed yields reproducibly and reversibly the vacancy equilibrium concentration. Figure 4 shows the vacancy concentration as a function of the annealing time at 1100 °C under two different As vapor pressures (0.1 and 5.6 atm). For the high As vapor pressure the vacancy concentration is constant at $\sim10^{17}$ cm^{-3}. Annealing at the lower As vapor pressure reduces the vacancy concentration within ~120 min to 2.2×10^{16} cm^{-3}. The samples annealed for long times at $p_{As}=0.1$ atm showed an increase in the carrier concentration, compatible with a reduction of the compensation through a reduced V_{Ga} concentration. This excludes the influence of unwanted impurities on our results. Obviously, annealing for a sufficiently long time establishes stationary conditions. Further annealing of the samples with low vacancy concentrations at higher As vapor pressure again restores the vacancy concentration of 10^{17} cm^{-3}. Thus the vacancy concentration can be reversibly adjusted by changing the As vapor pressure and the annealing indeed allows us to reach the thermal equilibrium concentration of Ga vacancies.

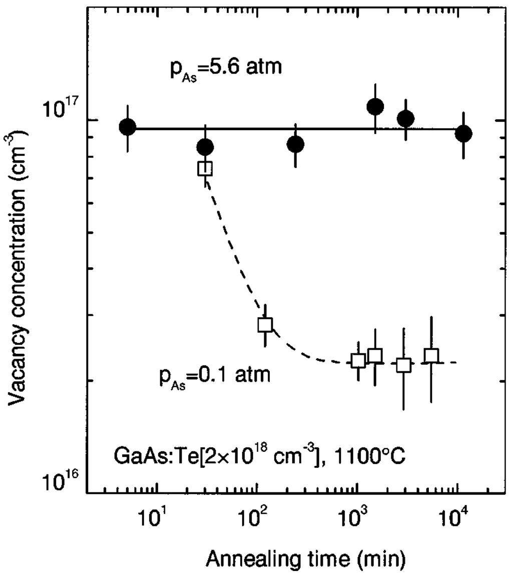

FIG. 4. Vacancy concentration in Te-doped GaAs ($[Te]=2\times10^{18}$ cm^{-3}) as a function of the annealing time at 1100 °C for arsenic vapor pressures of 5.6 (●) and 0.1 (□) atm. The lines are drawn guide the eye. The error bars reflect the uncertainty in the measurement of the average positron lifetime as in all following figures unless otherwise noted.

Figure 4 demonstrates that the vacancy concentration depends sensitively on the external As vapor pressure, raising the question as to which mechanism leads to various defect concentrations. Since we probe the bulk by positron annihilation, we need to consider indiffusion and outdiffusion of point defects from the surface to the crystal interior. The diffusion time t_D (120 min) and the average diffusion length L_D of 275 μm (corresponding to the half of the sample thickness) yields a diffusion coefficient D of 2.6×10^{-8} cm^2 s^{-1} at 1100 °C using $L_D = 2(D\,t_D)^{1/2}$. This value is in good agreement with the diffusion coefficient of Ga vacancies at 1100 °C, $D(V_{Ga}) \geqslant 1.5\times10^{-8}$ cm^2 s^{-1} (Ref. 33). This indicates that *isolated* Ga vacancies and not V_{Ga}-Te_{As} complexes establish the equilibrium with the As vapor pressure at elevated temperatures, because diffusion of the V_{Ga}-Te_{As} *complexes* is expected to be much slower, as it requires corre-

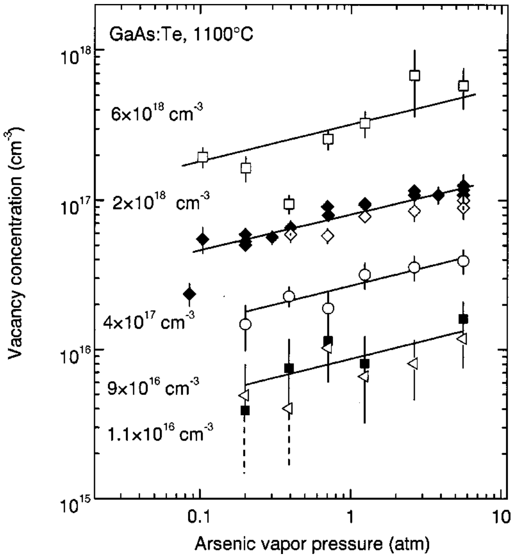

FIG. 5. Vacancy concentration in Te-doped GaAs as a function of the As vapor pressure during annealing at 1100 °C for 24 h. The Te concentrations are indicated. Open diamonds for $[\mathrm{Te}]=2\times10^{18}\ \mathrm{cm}^{-3}$ are from samples previously annealed at $p_{\mathrm{As}}=0.2$ atm, confirming the reversibility of the annealing. Lines are fits to a power law $c_v \sim p_{\mathrm{As}}^n$, yielding $n=(0.25\pm0.02)$.

lated jumps on both sublattices.[33] The presence of isolated Ga vacancies at high temperatures implies that the V_{Ga}-$\mathrm{Te}_{\mathrm{As}}$ complexes are dissociated. This is conceivable in view of an expected binding energy between donors and V_{Ga} of about 1 eV (Ref. 32). Irradiation-induced Ga vacancies in GaAs anneal around 300 K (Refs. 34 and 35), implying that Ga vacancies are mobile already at low temperatures. Thus, upon cooling to 300 K, the isolated V_{Ga} migrate until they reach available sinks. The most numerous sinks are the positively charged $\mathrm{Te}_{\mathrm{As}}$ donors, which attract the negatively charged V_{Ga} due to their Coulomb interaction. Indeed, the vast majority of vacancies will be trapped at room temperature at the dopant atoms, because these have an average distance of only 46 nm compared to distances of at least 30 μm for external surfaces and dislocations (λ dislocation density of $5\times10^4\ \mathrm{cm}^{-2}$ was measured by scanning cathodoluminescence microscopy). Ga interstitials cannot act as recombination centers either, because the As vapor pressures we applied yield As-rich GaAs (Ref. 36), where Ga interstitials are not expected to occur. Therefore, we conclude that the concentration of V_{Ga}-$\mathrm{Te}_{\mathrm{As}}$ complexes measured at room temperature by PA is equal to that of isolated V_{Ga} present in equilibrium at high temperatures, as all vacancies will be trapped at dopant atoms.

Figure 5 shows the vacancy concentration as a function of the As vapor pressure for different doping concentrations after annealing at 1100 °C for 24 h. First, for all doping concentrations the vacancy concentration increases with As vapor pressure: i.e., when the material becomes more As rich. This dependence on the As vapor pressure can be understood when considering that Ga vacancies are formed by the incorporation of As from the As_4 gas phase following the reaction $\frac{1}{4}\,\mathrm{As}_4^{\mathrm{gas}} \leftrightarrow V_{\mathrm{Ga}}+\mathrm{As}_{\mathrm{As}}$ (Ref. 33). According to the mass action law, the equilibrium concentration of V_{Ga} must then be proportional to $p_{\mathrm{As}}^{1/4}$. Indeed, all data sets can be fitted well by a power law $c_v \sim p_{\mathrm{As}}^{0.25\pm0.02}$ (solid lines in Fig. 5). Thus our data support the reaction model above. This result also corroborates the interpretation in terms of Ga vacancies: furthermore, it is in accordance with the conclusion that the vacancy concentration has reached thermal equilibrium. Figure 5 also shows that the vacancy concentration increases with the doping concentration for all As vapor pressures.

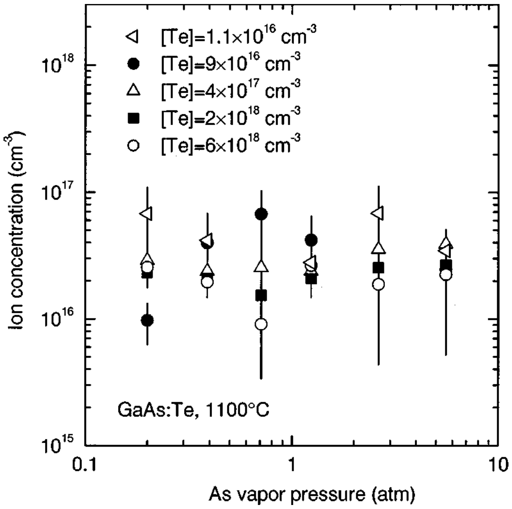

FIG. 6. Concentration of acceptor-type ions in GaAs:Te as a function of the As vapor pressure during annealing at 1100 °C for 24 h. The Te concentrations are indicated.

D. Acceptor-type ions

At this stage, we need to address the occurrence of acceptor-type ions in our samples. Native acceptor-type ions are frequently found in GaAs by positron annihilation.[9,22,27,29,30] However, they can not be directly identified because the annihilation parameters are close to the bulk values. Acceptor-type ions could have an influence on the equilibrium concentration of the V_{Ga} acceptors because they influence the charge neutrality and thus the electronic part of the Gibbs free energy of formation. We address these questions by determining the concentration of negative ions as a function of doping and As vapor pressure.

At very low temperatures (~25 K), positrons cannot escape once they are trapped by the ions. Then the concentration of the ions, c_{ion}, can be determined from a two-defect trapping model without considering detrapping. The trapping rate κ_{ion} of the ions is then

$$\kappa_{\mathrm{ion}}(25\ \mathrm{K}) = c_v\mu_v(25\ \mathrm{K})\,\frac{\tau_v-\tau_{\mathrm{av}}(25\ \mathrm{K})}{\tau_{\mathrm{av}}(25\ \mathrm{K})-\tau_{\mathrm{bulk}}} - \tau_{\mathrm{bulk}}^{-1}$$

$$= \mu_{\mathrm{ion}}(25\ \mathrm{K})c_{\mathrm{ion}}, \qquad (2)$$

where μ_{ion} is their trapping coefficient.[9] We use the common assumption that the positron lifetime at the ions is equal to τ_{bulk}. The trapping coefficients at 25 K are $5\times10^{16}\ \mathrm{s}^{-1}$ for the ions and $1.5\times10^{16}\ \mathrm{s}^{-1}$ for the vacancies, respectively.[37]

Figure 6 shows that the ion concentration extracted from the PA data is independent of the As vapor pressure and the particular doping concentration. Intrinsic defects such as

$\mathrm{Ga_{As}}^{2-}$ antisites or As_i^{-} interstitials can thus be ruled out: their concentration would vary with the external chemical potential—i.e., with the As vapor pressure. Therefore, the acceptor-type ions detected by us are extrinsic impurities. Based on these and earlier results which allowed a clear identification by a reference method,[30] we suggest that all native acceptor-type ions detected by PA are extrinsic impurities. A likely assignment for our samples are $\mathrm{C_{As}}$ or $\mathrm{Cu_{Ga}}$ acceptors. These acceptors might have been unintentionally[15] introduced during annealing, the concentration of acceptor-type ions in the as-grown material was considerably lower ($<10^{16}\ \mathrm{cm}^{-3}$) than in the annealed samples.[19,23]

The ion concentration in Fig. 6 is constant at $\sim 3\times 10^{16}\ \mathrm{cm}^{-3}$. This is lower than the vacancy concentration for high doping concentrations ($[\mathrm{Te}]\geqslant 4\times 10^{17}\ \mathrm{cm}^{-3}$) and the As vapor pressure of 5.6 atm. For the lowest doping concentrations ($\leqslant 9\times 10^{16}\ \mathrm{cm}^{-3}$), the ion concentration is similar to that of V_{Ga}. The negative ions compensate an equal amount of donors. Consequently, we consider their influence by adjusting the absolute donor concentration to an effective value in the following calculations. This effective value is given by the difference between the total donor concentration and the concentration of negative ions calculated for a given sample. It is shown below that the negative ions have no influence on our result for the Gibbs free energy of formation of the Ga vacancy.

IV. GIBBS FREE ENERGY OF FORMATION

Before we are able to determine the Gibbs free energy of formation we first need to develop a model with help of the measured temperature dependence of the vacancy concentration. For the determination of the temperature dependence, the samples were first annealed at 1100 °C to establish common starting conditions, slowly cooled (20 K/h) to the desired temperature, and then annealed. We investigated two different As vapor pressures (2.5 and 5.6 atm) to ensure the reproducibility of the results. Figure 7 shows that the vacancy concentration *decreases* slightly with increasing temperature. At first sight this observation is surprising as one may expect the opposite effect—i.e., an exponential increase, according to $c_v \sim \exp(-G_f/k_B T)$ where k_B is the Boltzmann constant. At a closer look, this can be understood as follows: The equilibrium concentration of Ga vacancies in GaAs is[12,20]

$$c_v=(p_{\mathrm{As}}/B_{\mathrm{As}})^{1/4}\exp[-(H_f-T\ S_f)/k_B T]. \tag{3}$$

$B_{\mathrm{As}}=(135.1T^{5/2})$ atm is the gas pressure constant for $\mathrm{As_4}$ vapor in equilibrium with the GaAs at the temperature T and $(H_f-T\ S_f)$ is the Gibbs free energy of formation of the Ga vacancy. The formation enthalpy H_f of a Ga vacancy with a charge $-ze$ is given by

$$H_f=H_f^0-(zE_F-\Sigma E_{a,i}), \tag{4}$$

with H_f^0 being the formation enthalpy of the uncharged Ga vacancy. E_F is the position of the Fermi level and $E_{a,i}$ the ith ionization level of V_{Ga} ($i\in\{0 \text{ to } z\}$), both relative to the valence-band edge. The term in the bracket in Eq. (4) is the electronic energy gained by binding electrons in the vacancy levels. This energy gain is largest if the Fermi level is close to the conduction band. With increasing temperature E_F moves, however, toward the middle of the band gap due to the increasing concentration of intrinsic carriers, thus increasing the formation enthalpy H_f. Therefore, the equilibrium vacancy concentration described by Eq. (3) can decrease under certain circumstances with increasing temperature, because H_f increases.[12,20] This is what we observed and we provide here experimental proof for such a so called "negative temperature dependence" predicted in Ref. 20.

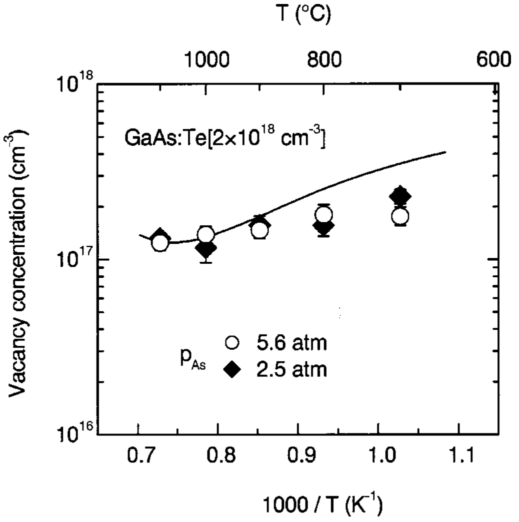

FIG. 7. Temperature dependence of the vacancy concentration in Te-doped GaAs ($[\mathrm{Te}]=2\times 10^{18}\ \mathrm{cm}^{-3}$) for As vapor pressures of 5.6 and 2.5 atm. The solid line is a calculation for a vacancy charge of $-3e$ (see text).

We can now model the dependence of the vacancy concentration on temperature and doping concentration using Eqs. (3) and (4). Here c_v is calculated for a given electron concentration n_e using the relation $c_v(n_e)/c_v(n_i)=(n_e/n_i)^z$, where n_i is the intrinsic carrier concentration.[20] The vacancy concentration $c_v(n_i)$ in intrinsic GaAs is obtained by using the intrinsic Fermi level $E_F(n_i)$ in Eq. (4). All dopants are assumed to be electrically active and the ionization levels $E_{a,i}$ vary with the temperature proportional to the band gap E_G (Ref. 20). The temperature dependence of the band gap, the intrinsic Fermi level $E_F(n_i)$, and the intrinsic carrier concentration n_i are taken from Ref. 38. The concentration of V_{Ga} in all charge states (i.e., from 0 to $-3e$) is summed up. We restrict the analysis in such a way that the formation enthalpy H_f for the charged V_{Ga} [given by Eq. (4)] in intrinsic GaAs agrees with the value $H_f^{\mathrm{intrinsic}}=1.9$ eV obtained from the analysis of diffusion experiments. $H_f^{\mathrm{intrinsic}}$ for V_{Ga} is given by the difference between the migration enthalpy of 1.8 eV (Ref. 39) and the activation enthalpy of 3.7 eV of Ga self-diffusion in undoped GaAs.[40]

From the simultaneous analysis of doping and temperature dependence of the V_{Ga} concentration (solid lines in Figs. 7 and 8, respectively), we obtain the formation entropy S_f

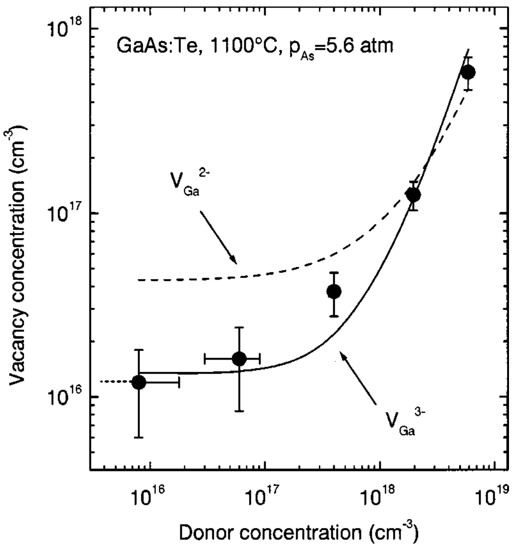

FIG. 8. Equilibrium Ga vacancy concentration at 1100 °C in Te-doped GaAs as a function of the doping concentration. Calculations using $p_{\mathrm{As}}=5.6$ atm and $T=1100$ °C are shown for a vacancy charge of $-2e$ (dashed line) and $-3e$ (solid line). The error bars for the Te concentration are due to uncertainties imposed by negative ions (see text). Note that these uncertainties are smaller than the symbol size for doping concentrations above 10^{17} cm^{-3}.

$=(9.6\pm1)k_B$ and the formation enthalpy $H_f^0=(3.2\pm0.5)$ eV of the uncharged Ga vacancy. The values of the formation enthalpy of charged vacancies, $H_f^{z\neq0}$, can be deduced using Eq. (4) as a function of E_F. The agreement between the fit and experimental data is very good with the exception of the two lowest temperatures in Fig. 7. We suggest that these samples have not fully reached thermal equilibrium because, at these considerably low temperatures, the formation of vacancy complexes and slow Ga self-diffusion will delay the establishment of equilibrium conditions. Therefore, the measured vacancy concentration is in that case a lower limit of the true equilibrium concentration. The error ranges are estimated by a systematic sampling of the various fit parameters. Note that the donor concentration in Fig. 8 is the effective value, defined in Sec. III D as the difference between Te concentration and concentration of acceptor-type ions. The error for the donor concentration in Fig. 8 corresponds to the measured ion concentration. This uncertainty is significant only at doping concentrations below 10^{17} cm^{-3} (horizontal error bars in Fig. 8). For these low doping concentrations, however, the carrier concentration at the annealing temperature of 1100 °C is determined by the intrinsic carrier concentration [$\sim10^{18}$ cm^{-3} (Ref. 38)]. Thus the equilibrium V_{Ga} concentration is constant and does not depend on the Te doping concentration. The uncertainties imposed by acceptor-type ions have clearly no influence on our results.

A separate analysis is performed for $-2e$- and $-3e$-charged V_{Ga}. Good agreement with the experimental data is only obtained for a $-3e$ charge (solid lines in Figs. 7 and 8). In the analysis, we use the ionization levels $E_a(0/1-)=0.13E_G$, $E_a(1-/2-)=0.35E_G$, and $E_a(2-/3-)=0.49E_G$ as calculated in Ref. 6. We note that information about the exact positions of the ionization levels cannot be obtained from our data because only the sum over $E_{a,i}$ is relevant in Eq. (4). More recent calculations obtained shallower ionization levels than those above.[5,7] However, experimental values obtained in electron-irradiated GaAs (Refs. 41 and 42) or from the analysis of Schottky barrier heights[43] support our assignment of deeper-lying levels. Agreement with the experimental data could not be obtained if the third ionization level is omitted: i.e., if V_{Ga} were only twofold negatively charged (dotted line in Fig. 8: the ionization levels are those obtained in Ref. 2). Therefore, our results are only compatible with a $-3e$ charge of V_{Ga}. This agrees with theoretical expectations[5–7] and experimental results on nonstoichiometric GaAs layers,[44] but disagrees with the interpretation of recent diffusion experiments in Si-doped GaAs (Ref. 2), where a $-2e$ charge was obtained. We attribute this discrepancy to the omission of $\mathrm{Si_{As}}^-$ acceptors and Si clusters present in the Si- but not Te-doped GaAs (Refs. 14–17) in the data analysis in Ref. 2.

A formation enthalpy $H_f^{\mathrm{intrinsic}}$ of 4 eV and a formation entropy of $32.9k_B$ has been estimated earlier for V_{Ga} from interdiffusion of Si-doped AlGaAs/GaAs heterostructures (no attempt to determine H_f^0 and the charge state separately was undertaken).[1] These values are larger than the currently accepted value $H_f^{\mathrm{intrinsic}}=1.9$ eV and our result $S_f=(9.6\pm1)k_B$. This is presumably caused by the low temperatures (600–650 °C) used, where V_{Ga}-$\mathrm{Si_{Ga}}$ complexes should not be dissociated. Hence a reduced diffusivity and a larger activation enthalpy for diffusion can be expected. More recently, Mitev *et al.*[45] have obtained a formation enthalpy of (1.8 ± 0.5) eV and a formation entropy of $(5.2\pm5.7)k_B$ from interdiffusion on AlGaAs/GaAs heterostructures. The parameters were not properly defined according to Eqs. (3) and (4), and a relationship to doping and charge state of V_{Ga} was not established, making these results difficult to compare to ours. Moreover, the very low V_{Ga} equilibrium concentration estimated[45] (only 5.2×10^{15} cm^{-3} in highly *n*-doped GaAs) is at variance with our results (e.g., Fig. 8). Recent self-diffusion experiments in isotopically controlled GaAs layers have shown that Ga self-diffusion is not adequately described by Ga-Al interdiffusion, which might explain the differences.[40] On the other hand, Bockstedte and Scheffler[3] determined the Gibbs free energy of formation of V_{Ga} using first-principles calculations. They obtained $H_f^0=2.8$ eV and $S_f=7.3k_B$, in good agreement with our experimental results of $H_f^0=(3.2\pm0.5)$ eV and $S_f=(9.6\pm1)k_B$. Other first-principles calculations yielded $H_f^0=3.5$ eV (Ref. 32), also in reasonable agreement with our experiments.

V. SUMMARY

We investigated equilibrium Ga vacancies in *n*-doped GaAs:Te by positron annihilation. From a simultaneous analysis of the doping and temperature dependence of the Ga vacancy equilibrium concentration, we obtained the Gibbs free energy of formation of the Ga vacancy to be $G_f=[3.2\text{ eV}-(z\,E_F-\Sigma E_{a,i})-T\times9.6k_B]$. Our results point to a $-3e$ charge of the Ga vacancy in *n*-doped GaAs, with ionization levels $E_{a,i}$ of $E_a(0/1-)=0.13E_G$, $E_a(1-/2-)=0.35E_G$, and $E_a(2-/3-)=0.49E_G$. Here $H_f^0=(3.2\pm0.5)$ eV was found to be the formation enthalpy of the neutral V_{Ga} and $S_f=(9.6\pm1)k_B$ the formation entropy. Finally, we note that our methodology can be easily applied to other semiconductor materials. Similar experiments may therefore significantly increase knowledge about the fundamental thermodynamic properties of vacancies in semiconductors.

ACKNOWLEDGMENTS

We like to thank M. Jurisch (Freiberger Compound Materials GmbH) for providing the Te-doped GaAs material. G. Lippold (University Leipzig) is thanked for Hall effect measurements. J.G. acknowledges financial support from the Alexander von Humboldt foundation during his stay in Berkeley. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

---

*Electronic address: JGebauer@lbl.gov

[1] J.-L. Rouviere, Y. Kim, J. Cunningham, J. A. Rentschler, A. Bourret, and A. Ourmazd, Phys. Rev. Lett. **68**, 2798 (1992).
[2] H. Bracht, M. Norseng, E. E. Haller, K. Eberl, and M. Cardona, Solid State Commun. **112**, 301 (1999).
[3] M. Bockstedte and M. Scheffler, Z. Phys. Chem. (Munich) **200**, 195 (1997).
[4] U. M. Gösele and T. Y. Tan, in *Electronic Structure and Properties of Semiconductors*, edited by W. Schröter (VCH, Weinheim, 1991).
[5] R. W. Jansen and O. F. Sankey, Phys. Rev. B **39**, 3192 (1989).
[6] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 1327 (1985).
[7] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
[8] R. M. Cohen, Mater. Sci. Eng., R. **20**, 167 (1997).
[9] R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors* (Springer, Berlin, 1999).
[10] J. Throwe, T. C. Leung, B. Nielsen, H. Huomo, and K. G. Lynn, Phys. Rev. B **40**, 12 037 (1989).
[11] S. Dannefaer, P. Mascher, and D. Kerr, Phys. Rev. Lett. **56**, 2195 (1986).
[12] T. Y. Tan, Mater. Sci. Eng., B **10**, 227 (1991).
[13] T. Y. Tan, J. Phys. Chem. Solids **55**, 917 (1994).
[14] J. Gebauer, E. R. Weber, N. D. Jäger, K. Urban, and P. Ebert, Appl. Phys. Lett. **82**, 2059 (2003).
[15] D. T. J. Hurle, J. Appl. Phys. **85**, 6957 (1999).
[16] C. Domke, P. Ebert, M. Heinrich, and K. Urban, Phys. Rev. B **54**, 10 288 (1996).
[17] R. C. Newman, Semicond. Sci. Technol. **9**, 1749 (1994).
[18] J. Gebauer, M. Lausmann, F. Redmann, and R. Krause-Rehberg, Physica B **273–274**, 705 (1999).
[19] J. Gebauer, R. Krause-Rehberg, M. Lausmann, and G. Lippold, Mater. Sci. Forum **258–263**, 905 (1997).
[20] T. Y. Tan, H. M. You, and U. M. Gösele, Appl. Phys. A: Solids Surf. **56**, 249 (1993).
[21] N. A. Gokcen, Bull. Alloy Phase Diagrams **10**, 11 (1989).
[22] R. Krause-Rehberg, H. S. Leipner, A. Kupsch, A. Polity, and T. Drost, Phys. Rev. B **49**, 2385 (1994).
[23] J. Gebauer, M. Lausmann, T. E. M. Staab, R. Krause-Rehberg, M. Hakala, and M. J. Puska, Phys. Rev. B **60**, 1464 (1999).
[24] J. Gebauer, R. Krause-Rehberg, and T. E. M. Staab, Phys. Status Solidi B **220**, R1 (2000).
[25] M. Alatalo, H. Kauppinen, K. Saarinen, M. J. Puska, J. Mäkinen, P. Hautojärvi, and R. M. Nieminen, Phys. Rev. B **51**, 4176 (1995).
[26] J. Gebauer, R. Krause-Rehberg, S. Eichler, and F. Börner, Appl. Surf. Sci. **149**, 110 (1999).
[27] K. Saarinen, P. Hautojärvi, A. Vehanen, R. Krause, and G. Dlubek, Phys. Rev. B **39**, 5287 (1989).
[28] M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).
[29] C. Le Berre, C. Corbel, K. Saarinen, S. Kuisma, P. Hautojärvi, and R. Fornari, Phys. Rev. B **52**, 8112 (1995).
[30] J. Gebauer, R. Krause-Rehberg, C. Domke, P. Ebert, and K. Urban, Phys. Rev. Lett. **78**, 3334 (1997).
[31] H. Kauppinen, L. Baroux, K. Saarinen, C. Corbel, and P. Hautojärvi, J. Phys.: Condens. Matter **9**, 5495 (1997).
[32] J. E. Northrup and S. B. Zhang, Phys. Rev. B **47**, 6791 (1993).
[33] T. Y. Tan, U. Gösele, and S. Yu, Crit. Rev. Solid State Mater. Sci. **17**, 47 (1991).
[34] C. Corbel, F. Pierre, K. Saarinen, P. Hautojärvi, and P. Moser, Phys. Rev. B **45**, 3386 (1992).
[35] A. Polity, F. Rudolf, C. Nagel, S. Eichler, and R. Krause-Rehberg, Phys. Rev. B **55**, 10467 (1997).
[36] J. R. Arthur, J. Phys. Chem. Solids **28**, 2257 (1967).
[37] R. Krause-Rehberg and H. S. Leipner, Appl. Phys. A: Mater. Sci. Process. **64**, 457 (1997).
[38] J. S. Blakemore, J. Appl. Phys. **53**, R123 (1982).
[39] I. Lahiri, D. D. Nolte, M. R. Melloch, J. M. Woodall, and W. Walukiewicz, Appl. Phys. Lett. **69**, 269 (1996).
[40] H. Bracht, E. E. Haller, K. Eberl, and M. Cardona, Appl. Phys. Lett. **74**, 49 (1999).
[41] Y. Q. Jia, H. J. v. Bardeleben, D. Stienvard, and C. Delerue, Phys. Rev. B **45**, 1645 (1992).
[42] W. O. Siyanbola and D. W. Palmer, Phys. Rev. Lett. **66**, 56 (1991).
[43] T. J. Drummond, Phys. Rev. B **59**, 8182 (1999).
[44] M. Luysberg, H. Sohn, A. Prasad, P. Specht, Z. Liliental-Weber, E. R. Weber, J. Gebauer, and R. Krause-Rehberg, J. Appl. Phys. **83**, 561 (1998).
[45] P. Mitev, S. Seshadri, L. J. Guido, D. T. Schaafsma, and D. H. Christensen, Appl. Phys. Lett. **73**, 3718 (1998).