Investigation of defects in gallium arsenide using positron annihilation

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Grown-in defects in undoped GaAs, silicon-doped GaAs, and cadmium-doped GaAs have been investigated by positron-lifetime measurements. Trapping by vacancylike defects is observed in both undoped and silicon-doped GaAs, while no trapping occurs in cadmium-doped samples. The positron lifetime in these samples is 220 ps. The lifetime of trapped positrons in undoped GaAs is 290 ps, while in silicon-doped GaAs it is 260 ps. The 290-ps lifetime component is interpreted to arise from a monovacancy-impurity complex and the 260-ps component from annihilation at a substitutional silicon site. Room-temperature measurements on samples isochronally annealed up to 750 °C show removal of defects in undoped GaAs at approximately 500 °C. At higher annealing temperatures a new defect is created which yields a lifetime of only 225 ps. Similar observations pertain to silicon-doped GaAs except that no annealing stage is evident at 500 °C. It is proposed that the thermally created defect is a gallium antisite defect. Measurements in the (20—300)-K temperature range show that the trapping rate of the positrons increases roughly exponentially with increasing temperature in contrast to the case of silicon. A thermally activated trapping mechanism is proposed with activation energies appropriate to the defect in question. For the gallium antisite defect the activation energy is approximately 200 meV, about 60 meV for the substitutional silicon site, and 40 meV for the monovacancy-impurity complex.

I. INTRODUCTION

The nature of native defects in compound semiconductors has been, and still is, a source of much controversy. Despite much effort there is generally not a clear consensus as to the physical nature of a defect and how it relates to an experimentally determined parameter. The main reason for this ambiguity is that the electron-paramagnetic-resonance (EPR) technique—which has proven to be very successful in the case of silicon—is only of limited value for the compound semiconductors due to fairly broad resonance lines. Other available experimental techniques are deep-level transient spectroscopy (DLTS), photoconductivity, and infrared absorption, i.e., methods which provide direct information on the *energy levels* of defects, but leave the question of the *physical nature* of a defect somewhat open to interpretation.

This state of affairs is in part a result of the greater variety of defects one may encounter in compound semiconductors as compared to silicon and germanium. Elemental defects include two basic types of vacancies, two or more types of interstitials, and finally, there can be antisite defects (e.g., a group-III atom occupying the normal position of a group-V atom).

Theoretical calculations of the deep levels of various defects allow the possibility of establishing a connection between experimentally determined energy levels and the physical nature of such defects. Such calculations have been undertaken in recent years, but as of now they are not yet sufficiently accurate for such a purpose. For example, Bernholc and Pantelides[1] calculated the neutral $V_{\mathrm{Ga}}T_2$ level to be only 0.02 eV above the valence band in GaAs, while Lin-Chung and Reinecke[2] found a value of 0.44 eV. Considering that the band gap in GaAs is 1.5 eV, the spread in calculated values is rather substantial. A further complexity which theoretical calculations have to deal with is the question of lattice relaxation, which may be substantial (relative to silicon) due to the partly ionic binding. Lin-Chung and Reinecke,[2] for example, found that a 5% outward relaxation around a gallium vacancy increases the T_2 level from 0.44 to 0.63 eV.

Prompted by the problems outlined above, we have applied the positron-annihilation technique to the investigations of the nature of defects in GaAs. This method is capable of yielding information primarily on vacancylike defects, but does not yield any information on the energy levels of a particular defect. The positron, being a positive particle, will tend to be in an interstitial position in the lattice in order to avoid the positive atom cores. This, in turn, means that the positron will have a tendency to become trapped by vacancylike defects. Having become trapped, the average electron density experienced by the positron will be lower than that in the bulk of the crystal and, consequently, the lifetime of the positron will be increased.[3,4] This method has been used to investigate monovacancies,[5] divacancies, and quadrivacancies[6,7] in silicon, defects in deformed silicon,[8] and defects in amorphous silicon.[9]

Defects in GaAs have been studied previously. Cheng *et al.*[10] investigated undoped and doped GaAs and found that annealing around 250—300 °C resulted in a decrease of the mean lifetime. No evidence for the formation of arsenic vacancies could be found even after annealing at 1000 °C in vacuum. They also found that electron irradiation resulted in an increase of the mean lifetime. Kuramoto *et al.*[11] found that deformation increased the

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intensity of a long-lived component already present in the undeformed samples. Bharathi *et al.*[12] investigated GaAs heavily doped with silicon and found that the mean lifetime increased with increasing temperature. They attributed this increase to decreasing scattering of positrons with impurities, thus increasing the rate of trapping into defects. Dannefaer[13] succeeded in separating two lifetime components in GaAs, thus making possible a more detailed analysis, and Kerr *et al.*[14] investigated these samples as a function of temperature. They found a substantial increase of the intensity of the long-lived component ($\sim$300 ps) with increasing temperature. All of these investigations have shown that the positron-annihilation method can provide information on the defect structures in semiconductors, and the method is not restricted to any particular requirements on the conductivity of the semiconductor as is the case for DLTS and EPR.

In this paper we have undertaken, as a first step, the investigation of grown-in defects in variously doped GaAs, as functions of both measuring temperature and annealing temperature. The work is an extension of our previous work[13,14] where the character of some grown-in defects was first established using positron annihilation. The temperature-dependent trapping rate, already observed by Kerr *et al.*,[14] has been investigated in greater detail in the temperature range 20—300 K.

In addition, some preliminary experiments were done using light irradiation to determine if a change in the charge state of the defects can be induced and observed using the positron-annihilation technique.

II. EXPERIMENTAL

GaAs single crystals (grown by the Czochralski method) were obtained from Cambridge Instruments, England, and were identical to samples used in a former work.[13] Three types of GaAs were investigated here: undoped GaAs with a carrier density of 2.5×10^{16} cm^{-3} (*n* type), Si-doped GaAs to a concentration of 10^{18}cm^{-3} (*n* type), and, finally, Cd-doped GaAs also to a concentration of 10^{18} cm^{-3} (*p* type). The positron-lifetime measurements were performed using a fast-fast lifetime spectrometer. Polished Pilot U plastic scintillators without the usual reflecting paint were attached to RCA 8575 photomultiplier tubes. The scintillators had a base diameter of 35 mm and a height of 35 mm, and the outermost 15 mm of the scintillators was tapered to an angle of 10°. Standard 583 Ortec constant fraction differential discriminators were used with ^{22}Na window settings of $\Delta E/E_{\max}=38\%$ for the annihilation γ-ray quanta and $\Delta E/E_{\max}=57\%$ for the starting γ-ray quanta. The setting of the energy windows was chosen such that the backscattering coincidences contributed only 0.2% to the lifetime spectrum.[15] The full width at half maximum (FWHM) of the resolution function was (285$\pm$5) ps during the entire course of the experiment. A 20-μCi source was employed througout the experiments. The source material (^{22}NaCl) was enclosed in 1-mg/cm^2 Al foil, and gave a coincidence rate of 60 counts/s for low-temperature measurements (detector distance 40 mm). For room-temperature measurements the detector separation was decreased by about 20 mm to obtain a coincidence rate of 170—200 counts/s. Each lifetime spectrum contained no less than 4×10^6 counts, and in several cases, 2×10^7 counts were accumulated.

The lifetime spectra were analyzed by first using the program RESOLUTION,[16] which determines the resolution-function parameters. Two Gaussians gave a very good fit to the resolution function; one Gaussian had a FWHM value of about 305 ps with an intensity of 80% (fixed-input value), while the other Gaussian, with an intensity of 20%, had a FWHM value of about 230 ps displaced by, at most, $\pm$10 ps from the main Gaussian. Upon determination of the resolution-function parameters for each individual lifetime spectrum, the spectrum was then analyzed by the POSITRONFIT EXTENDED program[16] using the already calculated resolution-function parameters. In this analysis, however, the source correction could be included. Since this source correction proved rather crucial in the analysis of some (albeit not all) of the lifetime spectra, the determination of this correction deserves some detailed comments.

The lifetimes in the source-correction spectrum arise from two processes. One is the annihilation in the aluminum foil which encapsulates the source material, and the other is the annihilation in the source material itself. It has already been found[13] that annihilation in the foil contributes with a lifetime of 250 ps having an intensity of 2.3% when in contact with GaAs. The contribution to the source component arising from the source itself will be specific to the actual source in question and was determined in this case from the following observations. When undoped, Si-doped, and Cd-doped GaAs were measured at 20 K and analyzed with a partial source correction corresponding to annihilation in the Al foil, it was found that, apart from a main lifetime component with 91% intensity, a second lifetime with a value of 410 ps and a 9% intensity was also present. In view of the fact (as we will see) that the lifetime spectra for the three types of GaAs differed substantially at higher temperatures, it appears that the second-lifetime component at low temperatures has a sample-independent origin, i.e., we attribute this component to the source. The total source correction hence becomes $\tau_1^S=250$ ps and $\tau_2^S=410$ ps with intensities of 2.3% and 9.0%, respectively. It should be mentioned that this source correction was determined from spectra with 2×10^7 counts in order to obtain very accurate lifetime and intensity values. Even so, the source correction is undoubtedly only approximate, resting primarily on the assumption that at very low temperatures (20 K) the 9%, 410-ps lifetime component is due to the source and not to the samples themselves. A check on this assumption was therefore made using only a 10-μCi source, and the 410-ps component was then reduced to 5%, indicating that this component arises from the source and not the samples themselves.

The annealing of the samples was performed in an oven with a helium-gas flow. At temperatures above 600 °C, a slight discoloration of the sample surfaces was evident. Polishing off this layer did not change the lifetime spectra, indicating that the layer was very thin. During the annealing the samples were only in contact with the inside

of an Al_2O_3 tube along the edges, while the flat and polished surfaces were free of any contact.

The light irradiation was performed using two 250-W infrared heating lamps. The light was "focused" on the samples by means of an aluminum cone with an exit dieter of 15 mm so that the sample surfaces were uniformly illuminated. The lowest photon energy impinging on the GaAs crystals was 0.45 eV (due to the cutoff of the glass window). Attenuation of the light was accomplished by inserting a metal grid in the light path rather than reducing the voltage on the lamps. The lowest sample temperature obtainable in this arrangement was 40 K since the radiation shroud in the cryostat had to be removed.

III. RESULTS

The isochronal-annealing results are shown in Figs. 1 and 2. All of these measurements were performed at room temperature and all show that the long-lived component τ_2 associated with trapping at defects stays roughly constant up to 450 °C and then decreases towards a value of only 225 ps. The intensity I_2 of this component showed a barely perceptible decrease around 275 °C (Fig. 1), a pronounced decrease in the 450–550 °C region, which was then followed by an increase to nearly 100% after annealing at 750 °C.

The behavior of the short-lived component τ_1 can be understood in terms of the simple one-stage trapping model.[3] According to this model, the shortest-lived component is a result of annihilation from the bulk of the material, that is, from a perfect site, but modified by the rate by which positrons are trapped by defects. The observed annihilation rate λ_1 $(=1/\tau_1)$ is given by

$$\lambda_1=\lambda_B+\kappa \; , \tag{1}$$

where λ_B is the bulk annihilation rate and κ is the trapping rate. From this model, one may further show that λ_B is given by

$$\lambda_B=\lambda_1 I_1+\lambda_2 I_2 \; , \tag{2}$$

where λ_2 is equal to $1/\tau_2$. All of the quantities on the right-hand side of Eq. (2) are observables permitting a calculation of λ_B. These calculated values should, of course, be constant, provided that both the model as well as the analysis is correct. With the use of the data presented in Figs. 1–5 the average value of λ_B was found to be (4.52 ± 0.06) ns^{-1}, corresponding to a bulk lifetime of (221 ± 3) ps, clearly showing a self-consistent analysis.

We would like to point out our initial concern as to the presence of the 225-ps τ_2 component with very high intensity as shown in Fig. 1. Since this is very close to the bulk lifetimes (220 ps, as it will be argued later), one may have been tempted to assign the 225 ps to the bulk lifetime, which, in turn, would mean that I_2 would be 0% and that no trapping at defects was occurring. Because this is a crucial point for our subsequent interpretation, the lifetime spectra corresponding to the 600, 650, and 750 °C annealing temperatures were accumulated to 2×10^7 counts

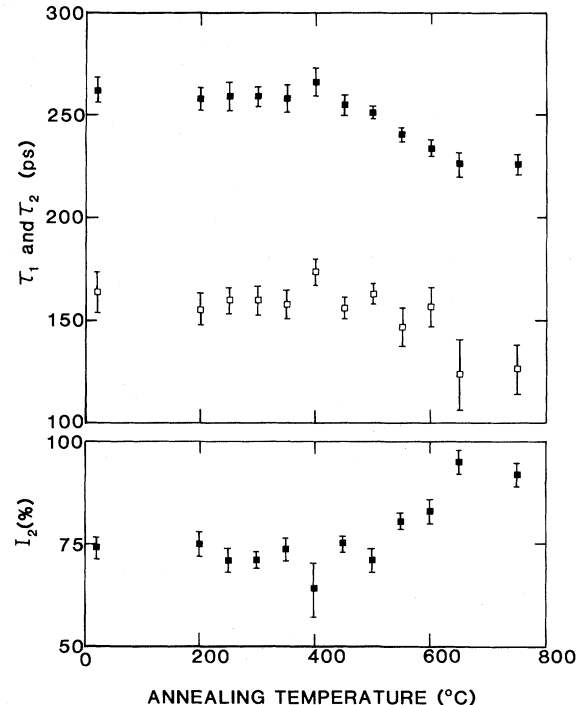

FIG. 2. Isochronal-annealing data for GaAs doped with 10^{18} Si at./cm^3. The samples were held at the temperature indicated for 1 h and measured at room temperature. τ_1 values are represented by open squares.

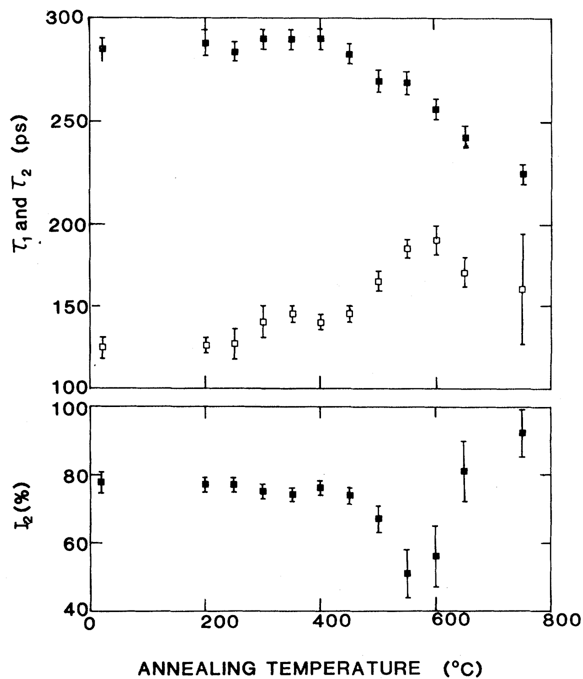

FIG. 1. Isochronal-annealing data for undoped GaAs. The samples were held at the temperature indicated for 1 h and measured at room temperature. τ_1 values are represented by open squares.

and analyzed assuming either one lifetime (which then should be the bulk lifetime) or two lifetimes. It turned out that if only one lifetime was assumed, the reduced χ^2 values were around 2.0 and showed persistent and clearly systematic deviations between fitted values and raw data. In the case of two lifetimes the χ^2 sum was very close to 1.0 and there were no systematic deviations. For this reason we maintain that trapping is indeed occurring despite the proximity of the τ_2 lifetime to the bulk lifetime. Furthermore, we point out that accumulation of the unusually high number of counts (2×10^7) in the lifetime spectra was necessary to reliably distinguish between the two possible interpretations.

It should be emphasized at this point that we of course do not claim to have been able to separate a 225-ps lifetime component in the presence of another 220-ps component (the bulk lifetime). It is only because of the reduction in the observed lifetime due to trapping [cf. Eq. (1)] that the 225-ps value can be resolved.

Another question which may be considered here is the possible influence from an incorrectly determined source correction. The source correction was essentially determined from low-temperature measurements and was considered to be temperature independent because of the temperature-independent lifetime in Cd-doped GaAs. Measurements on defect-free silicon in the (20—300) K range using the same source leads to the same conclusion and, most importantly, also yields a source correction

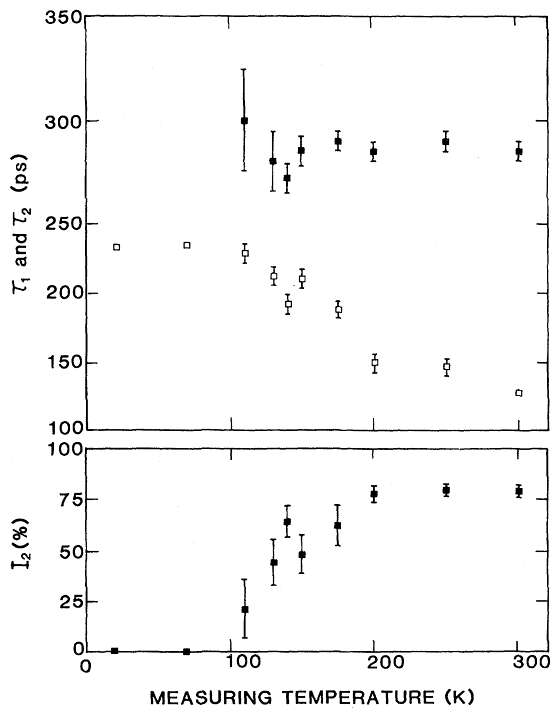

FIG. 3. Temperature dependence of lifetime spectra for unannealed and undoped GaAs. τ_1 values are represented by open squares.

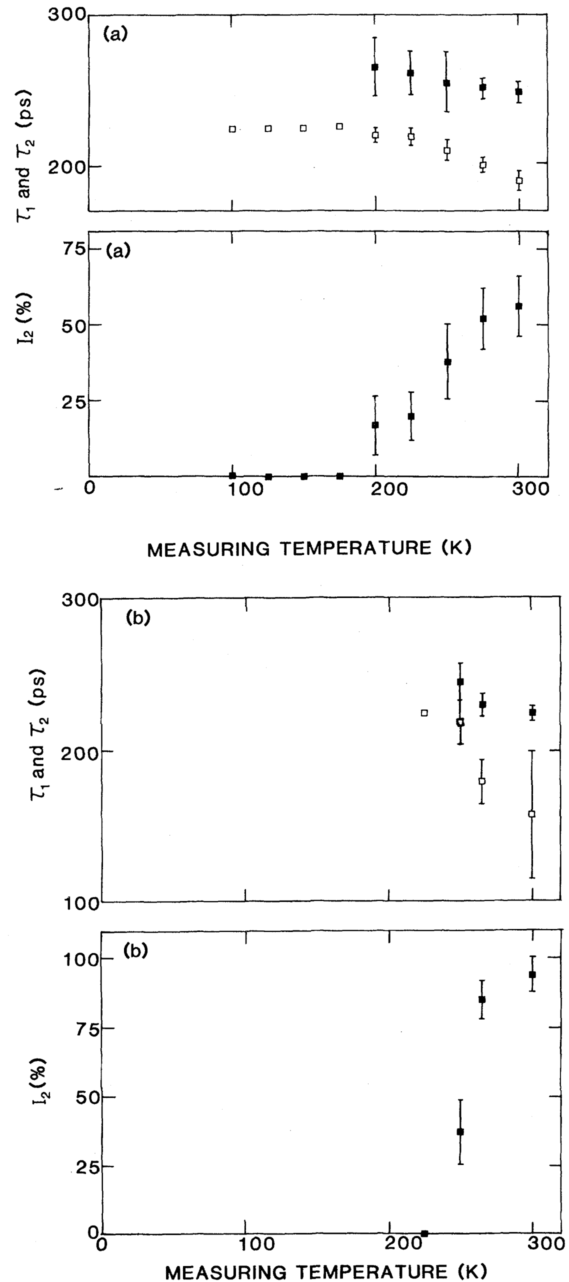

FIG. 4. (a) Temperature dependence of lifetime spectra for undoped GaAs subjected to a maximum isochronal-annealing temperature of 600 °C. (b) Same as (a) but for samples annealed up to 750 °C. τ_1 values are represented by open squares.

with 250- and 410-ps components (the intensities are slightly lower as expected due to the smaller atomic number of silicon). Still, we cannot claim that an incorrectly determined source correction could not have influenced the *value* of the 225-ps component, but the data certainly indicate the presence of two lifetimes in these lifetime spectra.

Figure 2 shows the results from similar annealing experiments on GaAs doped with 10^{18}-cm^{-3} silicon atoms. The value of τ_2 is again constant up to about 450 °C and

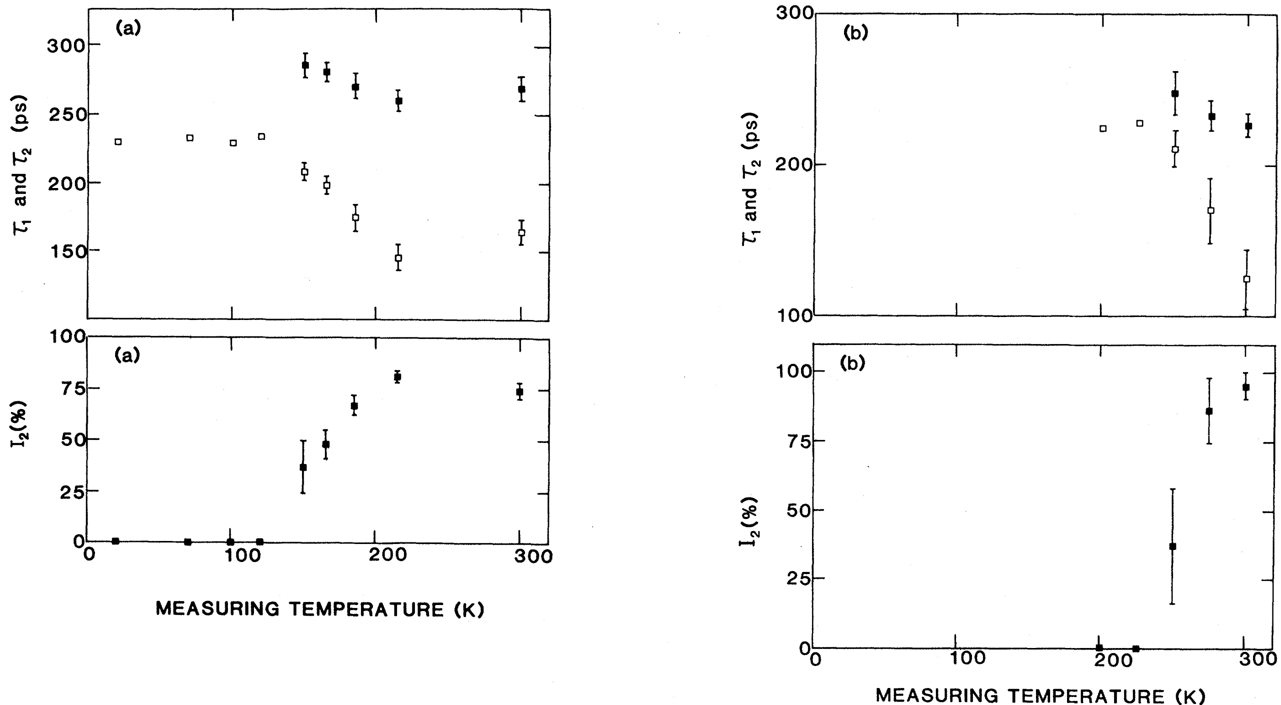

FIG. 5. (a) Temperature dependence of lifetime spectra for unannealed GaAs doped with 10^{18} Si at./cm^3. (b) Same as (a) but for samples annealed up to 650 °C. τ_1 values are represented by open squares.

then decreases towards 225 ps as was the case for undoped GaAs. It is noteworthy that I_2 does not show a decrease, but only an increase commencing at 500 °C.

Finally, annealing of GaAs doped with 10^{18}-cm^{-3} cadmium atoms showed that only one lifetime was present throughout the entire annealing program. This observation again is based on an analysis of lifetime spectra with 2×10^7 counts providing sufficient statistical accuracy to readily detect the presence of a second lifetime component. The mean value of the single lifetime was found to be (220±2) ps.

Lifetime spectra were also obtained as a function of measuring temperature in (20—300)-K range after different degrees of annealing. Figure 3 shows the results for undoped and unannealed GaAs, while Fig. 4 shows results obtained after the samples had been subjected to annealing at 600 and 750 °C. These results show that τ_2 is essentially temperature independent, while I_2 is reduced to zero at sufficiently low temperatures. The transition from maximum value to zero value occurs in a rather broad temperature range which, upon annealing at 600 and 750 °C, narrows and shifts toward higher temperatures. Similar observations pertain to Si-doped GaAs as shown in Figs. 5(a) (unannealed) and 5(b) (after annealing at 650 °C).

For Cd-doped GaAs no such temperature dependences could be found. At all measuring temperatures, both on unannealed as well as on 650 °C annealed samples, only one lifetime component could be observed with the aforementioned mean value of (220±2) ps.

A few crude experiments were also conducted using light irradiation. Samples were irradiated with visible as well as infrared radiation up to a wavelength of 2.5 μm. In Table I the lifetime results are collected and show that there indeed is an effect due to light irradiation in un-

TABLE I. Effect of light irradiation. ΔI_2 is defined as I_2(light)$-I_2$(no light). All samples were unannealed.

Measuring temperature (K)	Light Intensity (arb. units)	ΔI_2 (%) undoped GaAs	ΔI_2 (%) Si- and Cd-doped GaAs	τ_2 (ps) undoped GaAs
45	0.2	0±5		
45	0.5	23±9		285±26
45	1.0	86±5	0±2	251±3
90	1.0	45±12	0±2	278±14
150	1.0	0±10	0±2	

doped GaAs, while no effect could be determined in Si- and Cd-doped GaAs. The light irradiation increases the value of I_2 at low temperatures where one sees an increase from 0% to about 80%, while at higher temperatures the effect diminishes markedly. It should be noted that due to the positron source being sandwiched between the 1-mm-thick samples, light with an energy larger than the band-gap energy of ~ 1.5 eV would not penetrate to the region sampled by the positrons.

IV. DISCUSSION

Before considering the present results in detail it is worthwhile to examine the kinds of defects that might be expected, realizing that the defects observed in the present experiments are the remnants of the defects present during the growth of the samples. At high temperatures during growth conditions there would be a high concentration of Schottky-type vacancies just as in ionic crystals and, in addition, there will be impurities. As the temperature is reduced, the vacancy concentration decreases exponentially, but when the temperature becomes sufficiently low, trapping of vacancies by impurities will become important. If, for example, Ga vacancies are trapped by some impurity (and the system is still in thermal equilibrium), the concentration of As vacancies is lowered in order to maintain the product of the vacancy concentrations at its thermal-equilibrium value.[17] The concentration of vacancy-impurity complexes would, at maximum, be equal to the impurity concentration. As the temperature is lowered still, further thermal equilibrium is undoubtedly *not* maintained, so that a certain amount of Schottky defects is retained at room temperature. Further defects present at room temperature would be dislocations and—especially in doped materials—precipitates of impurities. Antisite defects would also be expected.[18,19]

It is also pertinent to describe briefly the state of the positron in perfect GaAs since it is from this state the positron is trapped by the defects. Through analogy with both silicon[20] and ionic crystals[21] we will expect the positron wave function to be peaked at interstitial positions, but there will be a tendency for this peak to be displaced towards the arsenic atoms since they have a negative charge.[22] Unfortunately, no theoretical calculations of the positron wave function have been performed for either free or trapped positrons in GaAs.

With these few general remarks we will now turn to the discussion of the positron data. The isochronal-annealing results, where all of the positron measurements were performed at room temperature, are considered first in Subsection A. Subsection B contains a discussion of the results obtained as a function of measuring temperature on samples subjected to different degrees of prior annealing. Finally, Subsection C deals briefly with the effects arising from light irradiation.

A. Isochronal-annealing results

It is simplest to begin with a consideration of the data for Cd-doped GaAs, since only one lifetime was observed having a value of (220 ± 2) ps up to an annealing temperature of 750 °C. The fact that only one lifetime could be detected agrees with our former work[13] using samples from the same batch, but disagrees with the previous value of (233 ± 1) ps. In fact, a substantial disagreement also exists in the case of the results for Si-doped GaAs but not in the case of undoped GaAs. Because of the good agreement for undoped GaAs it would appear that the discrepancies are not a matter of systematic errors (e.g., incorrect source correction) but rather that *the samples have changed during the three-year time span between the two sets of experiments,* a view supported by the now established aging of doped silicon.[23] The fact that the single lifetime of 220 ps was independent of both annealing and measuring temperature, in contrast to the results for the other samples, points to the suggestion that this lifetime could be associated with the bulk lifetime characteristic for GaAs. A further argument for this interpretation arises from the fact that Cd-doped GaAs is *p* type; thus many defects would be in a positively charged state and would therefore not constitute traps for the positively charged positron. This 220-ps value for the bulk lifetime is shorter by about 20 ps than the previously calculated value,[13] but we feel that this new value, as based on a wider body of experimental data, at least better approximates the true value.

The annealing results for undoped and Si-doped GaAs (Figs. 1 and 2) are strikingly different from those found by Cheng *et al.*[10] They observed a sharp decrease of the *mean* lifetime (i.e., they did not attempt a decomposition of the lifetime spectra) around 250 to 300 °C, followed by a slower decrease in the 300—500 °C range, using undoped GaAs of rather high purity. Significantly, another less pure sample showed the annealing step in the 250—300 °C range to be much reduced if not entirely removed. Although some care must be exercised in comparing simple mean-lifetime data and decomposed data, there is no question in this case that we do not observe the annealing stage at 250—300 °C in our experiments. Only at around 450 °C is annealing clearly evident for undoped GaAs.

It should be noted at this point that Cheng *et al.*[10] annealed their samples for 24 h in contrast to the 1-h anneals in this work. This, of course, would introduce a temperature discrepancy for a given annealing stage. However, if a first-order annealing process is assumed, it is easy to estimate the activation enthalpy consistent with the assumption that the 250—300 °C annealing and the 450 °C annealing arise from the same physical process. The result turns out to be ~ 0.5 eV, which is far too low a value for annealing at such high temperatures. For example, Farmer and Look[24] find that an annealing stage in electron-irradiated GaAs at 200 °C corresponds to an activation enthalpy of 1.2 eV. We must therefore conclude that two different defect configurations are responsible for the annealing stages. The difference is likely to arise from differences in impurity levels. Cheng *et al.*[10] observed the low-temperature stage at 275 °C for 1×10^{15} carriers/cm^3, none (or at least a much reduced stage) for 5×10^{15} carriers/cm^3, and we observed none for 2.5×10^{16} carriers/cm^3 (note that there is a misprint in the footnote to Table II in Ref. 13). Following the general considerations at the beginning of the discussion, this simply indi-

cates an increased number of vacancies associated with impurities (as opposed to free vacancies), which will reduce the amount of low-temperature annealing and increase the amount of high-temperature annealing. A more detailed comparison with the work of Cheng *et al.*[10] is not possible due to the difference in analysis of the lifetime spectra, and we therefore turn first to a further analysis of data for undoped GaAs.

In order to obtain a measure of the relative number of defects responsible for the τ_2 component, the trapping rate has been calculated on the basis of the simple trapping model.[3] This trapping rate is proportional to the concentration of defects, i.e.,

$$\kappa=\sum_i c_i \nu_i ,$$

where c_i is the concentration of the ith defect and ν_i is the corresponding specific trapping rate. The trapping rate may be calculated in two different ways from the experimental data,

$$\kappa=1/\tau_1-\lambda_B , \quad (3)$$

$$\kappa=I_2(\lambda_B-\lambda_2)/(1-I_2) . \quad (4)$$

Both methods of calculation should give the same results provided that both analysis (amounting principally to a proper resolution function and source correction) and model are correct. Trapping rates calculated from data shown in Fig. 1 are plotted in Fig. 6(a), and they exhibit as good a self-consistency as one may expect. In the temperature range up to 450 °C, κ exhibits a gradual decrease while τ_2 stays constant. This shows that only one dominant defect type contributes to τ_2 since, if this were not the case, τ_2 would have changed when κ changed. The value of τ_2 at less than 450 °C is 290 ps and is only 70 ps longer than the bulk lifetime, which is quite close to the increase (50 ps) observed for monovacancies in silicon.[5] This strongly suggests that the positrons annihilate in monovancies, and further, because of the high temperature at which the annealing stage occurs, that the monovacancies are associated with some impurity.[25] We may also conclude that there are no divacancies present in any appreciable concentration since their presence would result in a longer lifetime as was found for silicon.[6]

We have no direct evidence for which kind of monovacancy, i.e., $V_{\rm Ga}$ or $V_{\rm As}$, is present in the vacancy-impurity complex. We do expect, however, that $V_{\rm Ga}$ in its isolated form would be a positron trap. The reason for this expectation rests on theoretical calculations[1] which show that the neutral $V_{\rm Ga}$ defect introduces an energy level close to the top of the valence band, making it an acceptorlike defect. Thus, negatively charged states could conceivably be present in the band gap; such states have been calculated[26] to exist for GaP. For $V_{\rm As}$, the neutral defect level has been calculated to be close to the bottom of the conduction band.[1] This defect would therefore be donorlike and any charged states would tend to be positive. The actual charge state in either case would of course depend on the position of the Fermi level (or rather the chemical potential), but it is clear that $V_{\rm Ga}$ for any position of the Fermi level would be more attractive to the positron than for the

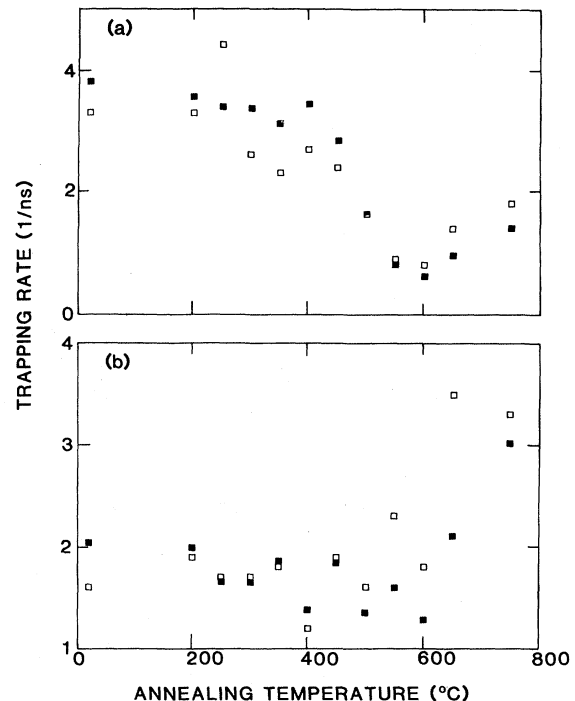

FIG. 6. (a) Trapping rate as a function of isochronal-annealing temperature for undoped GaAs. Closed squares signify calculated values based on Eq. (3), while open squares are calculated on the basis of Eq. (4). (b) Trapping rate as a function of isochronal-annealing temperature for GaAs doped with 10^{18} Si at./cm^3.

$V_{\rm As}$ defect. Unfortunately, these arguments may not be used to draw a firm conclusion as to the type of vacancy responsible for trapping since the defects here are not simple monovacancies but rather vacancy-impurity complexes.

In the earlier discussion of defects present after cool down of the GaAs, it was mentioned that dislocations could also be present, and we must therefore consider the possibility that dislocations could account for the presence of τ_2. This possibility cannot be disposed of on the basis of the value of τ_2 itself, since in silicon[8] it has been shown that dislocations may yield a lifetime close to that of monovacancies. However, by considering the data for deformed silicon,[8] where 10^7 dislocations cm^{-2} yielded a barely perceptible response, it appears that the dislocation concentration of $\sim 10^4$ cm^{-2} for the present samples[13] is too small to account for the τ_2 component.

Thus far we have only considered the annealing data for undoped GaAs up to 450 °C. At higher temperatures we first observe a rapid decrease of the trapping rate followed by a slight increase [Fig. 6(a)], but at the same time a smooth decrease in τ_2 occurs (Fig. 1). The combined behavior of τ_2 and κ at $T > 600$ °C suggests that a new defect is being introduced by the annealing, and that the lifetime corresponding to this defect is close enough to the 290-psec lifetime that some mean value emerges from the computer analysis. Examining the qualitative behavior of the trapping rate shown in Fig. 6(a), it appears that the

new defect type starts to be produced around 500 °C and that at 750 °C it is the dominant defect in which the positron has a lifetime of 225 ps.

Concerning the type of defect that could be produced during this high-temperature annealing, it is well known that arsenic evaporates from the surface of GaAs at high temperatures. It therefore seems natural to assume that arsenic vacancies are created. However, if such were the case and if the arsenic vacancies constituted positron traps, then, to be consistent with all other monovacancy lifetime data, the observed lifetime would have to be in the neighborhood of 290 ps. Instead, the value observed is only 225 ps. The absence of a long-lived component may be interpreted to mean that the arsenic vacancy is simply not an effective positron trap as discussed above. Alternatively, Chiang and Pearson[27] have argued, on the basis of self-diffusion data, that the depth of the arsenic deficiency layer may only be a few micrometers thick. The positron, which has an implantation depth of $\sim 100\ \mu$m, would therefore be relatively insensitive to such a thin layer of vacancies.

We are therefore led to propose the following defect reactions to explain the occurrence of the 225-ps lifetime component. At high temperatures ($T > 500\,^{\circ}$C), arsenic vacancies are created according to the reaction

$$\mathrm{As} \rightarrow V_{\mathrm{As}} + \mathrm{As}_i \ ,$$

where As_i signifies an interstitial As atom. At these temperatures both defects are highly mobile, especially so As_i, which is then lost to either internal traps or to the outer surfaces. As argued above, V_{As} is not the end product given the small value of τ_2. If we consider the additional reaction

$$V_{\mathrm{As}} + \mathrm{Ga} \rightarrow \mathrm{Ga}_{\mathrm{As}} + V_{\mathrm{Ga}} \ , \tag{5}$$

where $\mathrm{Ga}_{\mathrm{As}}$ is the Ga antisite defect and remember also that V_{Ga} is highly mobile so that disappearance of this defect could occur at, perhaps, dislocations, then the end product after cool down from the high-temperature annealing would simply be the $\mathrm{Ga}_{\mathrm{As}}$ antisite defect. This defect is expected to be an acceptor so that if the Fermi level were sufficiently high, it could be a positron trap. Obviously, the lifetime for positrons trapped at such a defect would be very close to that of the bulk if not for any other reason than the size of Ga and As being nearly the same. To our knowledge there is no independent evidence for the transformation proposed in Eq. (5), so the proposed reaction should only be viewed as a possibility which satisfies the positron-annihilation data.

Focusing our attention on the Si-doped GaAs we note that the lifetime after high-temperature annealing also approaches 225 ps (Fig. 2) and that the trapping rate [Fig. 6(b)] increases at $\sim 500\,^{\circ}$C. Both of these observations point to the formation of the same defect as in undoped GaAs, as indeed would have been expected, since the defect is thermally created. In Cd-doped GaAs we would also expect the formation of defects after high-temperature annealing, but since the Fermi level is close to the top of the valence band in these samples, the absence of a defect response indicates that the new defects are in a positively charged state.

Finally, a comparison of the annihilation parameters in undoped and Si-doped GaAs indicate three notable differences. The value of τ_2 in Si-doped GaAs is significantly less than in undoped GaAs, suggesting simply that the silicon occupies the vacancy. For this configuration the specific trapping rate would be expected to be reduced, which would lead to the reduction in κ as seen in Fig. 6. The absence of a clear annealing stage for Si-doped GaAs at 450 °C (Fig. 6) simply indicates a high thermal stability of the substitutional silicon.

B. Temperature dependence of lifetime spectra

The lifetime data's dependence on temperature is shown in Figs. 3—5, and the trapping rates calculated according to Eqs. (3) and (4) are shown in Figs. 7 and 8 where we again note a gratifying self-consistency between the two trapping-rate values. The Cd-doped GaAs data did not show any variation with temperature; only the 220-ps lifetime was present regardless of measurement or annealing temperature.

The reduction of the trapping rate to zero at sufficiently low temperatures as observed in undoped GaAs and Si-doped GaAs is exactly opposite to the behavior of silicon[6,7] and therefore indicates a fundamental difference in

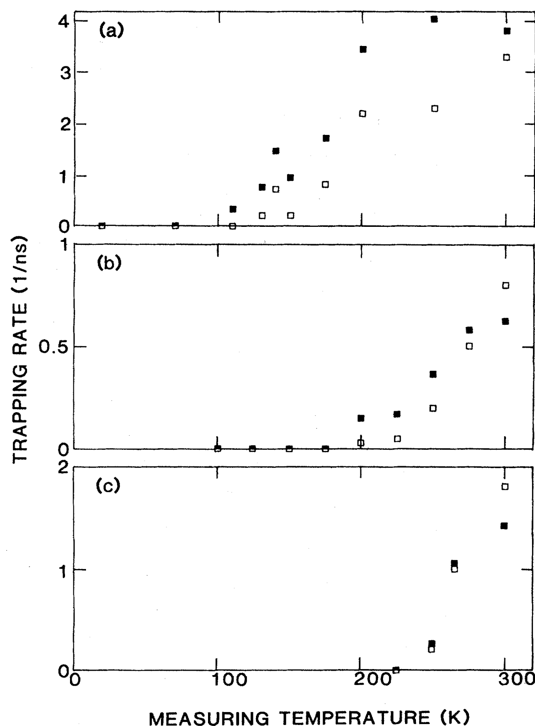

FIG. 7. (a) Trapping rate as a function of measuring temperature for undoped and unannealed GaAs. Closed and open squares are calculated from Eqs. (3) and (4), respectively. (b) Same as (a) but for samples annealed to 600 °C. (c) Same as (a) but for samples annealed to 750 °C.

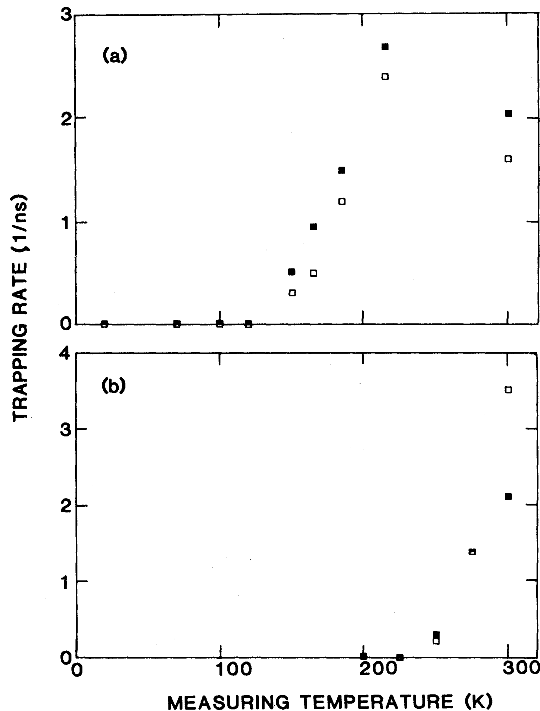

FIG. 8. (a) Trapping rate as a function of measuring temperature for GaAs doped with 10^{18} Si at./cm^3. Closed and open squares are calculated from Eqs. (3) and (4), respectively. (b) Same as (a) but for samples annealed to 650 °C.

the trapping mechanisms in GaAs and Si. Furthermore, since the temperature range in which the trapping rate changes from zero to its maximum value clearly depends on the prior annealing temperature (cf. Figs. 7 and 8), the trapping appears to be influenced by the defect itself. We observe that the shorter the lifetime of the trapped positron, the higher the transition-temperature range, suggesting that the trapping rate must be influenced by the atomic configuration very close to the defect. This suggestion is substantiated by Figs. 7(c) and 8(b) where the same defect, i.e., the proposed antisite defect, is responsible for the trapping, and the major change in κ is seen to occur over the same temperature range.

It is certainly remarkable that the trapping rate increases with increasing temperature in GaAs while it decreases in silicon. Several mechanisms accounting for this may be envisaged, and presently we can only point to the most likely one consistent with the present data, realizing, however, that future work is necessary to firmly establish the mechanism responsible. The possibilities we have considered are the following: multiphonon trapping process, polaron formation, positron—wave-function localization on the As sublattice, impurity scattering, and Fermi-level variation with temperature.

1. Multiphonon trapping process

This process is appealing since experimental and theoretical work by Henry and Lang[28] has already established that the trapping cross section for electrons and holes in GaAs can be explained in many cases by assuming that several phonons are emitted during trapping into deep levels. This leads to a trapping cross section of the form $\sigma=\sigma_{\infty}e^{-E/kT}$, and recent work by Poulin and Bourgoin[29] on Ge has also shown such a dependency. Now, if the multiphonon model is also applicable to positrons, the same type of behavior would be expected for both GaAs and Si, but since this is not the case, the multiphonon model is unacceptable.

A short digression is in order in connection with this point. The multiphonon process was considered by Henry and Lang[28] because of the basic question as to how an electron liberates its binding energy when being trapped by a deep level, i.e., a single level situated many phonon energies below the conduction band. Even though such a mechanism may operate in the case of electrons, there is no reason to believe that this should be true for positrons as well. The positron is an "alien" particle to the crystal, and the positron energy levels are not synonomous with those of the electrons. The positron may have a range of closely spaced energy levels to occupy when being trapped and hence there would be no need for a multiphonon-emission process.

2. Polaron formation

The positron will polarize the lattice locally as in ionic crystals[30] and hence could form a polaron state. Such a polaron state has been suggested[31] to explain tunneling in polar semiconductors and the absence thereof in homopolar semiconductors. The basic idea is that, in order to become trapped, the positron must leave its polarization cloud, which would constitute an energy barrier, and hence lead to a decrease in trapping rate with decreasing temperature. There is a serious objection to this mechanism. When the lifetime for a trapped positron is close to the bulk lifetime (as for Ga_{As}), the positron wave function would be only weakly localized, which would mean a small energy barrier for trapping. Therefore the transition temperature range would be lower for such traps than for traps yielding a longer lifetime. Although we in fact observe exactly the opposite trend, we cannot entirely rule out some polaron effect, but we believe that this is not the important mechanism.

3. Positron—wave-function localization on the As sublattice

Localization at one atom type (As) could prevent a transition into a defect by virtue of the surrounding cations (Ga). Lattice vibrations would clearly influence a transition into a defect and these vibrations would vary with defect type, being larger ("softer" lattice) at a given temperature around a vacancy than in the perfect lattice.[7,32] It would therefore be expected that trapping would occur down to lower temperatures when τ_2 is large (a "soft" lattice) and move up in temperature with shorter lifetimes (a "stiff" lattice). This agrees with the observed trends, and, significantly, this model also predicts the absence of any such effect in silicon.

4. Impurity scattering

Impurity scattering could reduce the trapping rate, but should then also be observed in silicon. Furthermore,

such scattering is predicted to result in approximately a $T^{-1.5}$ dependence,[33] which would be too slow a variation to be consistent with the rapid changes observed.

5. *Fermi-level variation with temperature*

In principle, a movement of the Fermi level with temperature can change the charge state of a given defect and hence the trapping rate. If we consider Si-doped GaAs, which is *n* type, a lowering of the temperature would raise the position of the Fermi level and hence would tend to leave more defects in a negative state, increasing the trapping rate, in contrast to our observations.

The discussion presented above has ruled out several physical models considered here to explain the experimental data. The model involving localization of the positron wave function at As ions is consistent with the experimental data but further study would be required to confirm its validity.

On the basis of the data shown in Figs. 7 and 8 one may calculate the activation energy for the trapping process. The trapping rate can be written as

$$\kappa = V_+ \sigma_+(T) c_D \ , \tag{6}$$

where $V_+ = (2kT/m_+)^{1/2}$ is the average thermal velocity of the positron, $\sigma_+(T)$ is the temperature-dependent trapping cross section, and c_D is the concentration of the defects responsible for the trapping. Assuming an exponential form of $\sigma_+(T)$, i.e., $\sigma_+(T) = \sigma_0 e^{-E/kT}$, we find good straight-line fits of $\ln(\kappa T^{-1/2})$, which is proportional to $\sigma_+(T)$, versus $1/T$.

In the case of undoped and unannealed GaAs where the predominant defect is expected to be the vacancy-impurity complex [Fig. 7(a)], the resulting activation energy E is 43 meV. For Si-doped GaAs, $E \sim 60$ meV, and for high-temperature-annealed GaAs, where the antisite defect should predominate [Figs. 7(c) and 8(b)], $E \sim 200$ meV.

These values are within the rather broad range of activation energies for multiphonon emission,[28,29,34] but in the light of the above discussion we do not believe that it has any relevance to this process being operative in the trapping of positrons. We rather envisage the various activation energies as barrier heights which are modified by the detailed atomic configuration around the different defects.

We may gain some insight into the highest value, $E \sim 200$ meV, in the case of the Ga_{As} defects, by noting that if the positron wave function is peaked around arsenic atoms, then in order to become trapped by a Ga_{As} defect it will have to "penetrate" through the shell of Ga atoms surrounding the Ga_{As} defect. Since the lattice relaxation is expected to be small around this defect, the value of 200 meV may be envisaged simply to be the binding energy of a positron to the arsenic atom (or more precisely the difference in Wigner-Seitz energies corresponding the positron bound to positive and negative ions[21]). The localization of the positron wave function proposed here seems to be substantiated by some angular correlation data,[35] although Mokrushin *et al.*[36,37] unexpectedly concluded that there does not appear to be a clear dependency on the ionicity of the bonding. The reason may be, as this work has indicated, that a very large amount of trapping is likely to occur in compound semiconductors at room temperature, hence diminishing effects from the bulk properties of the semiconductors. The fact that an activation energy is observed for trapping at Si_{As} defects at all is readily understood in terms of the above interpretation since, again, the positron has to "penetrate" a shell of Ga atoms in order to become trapped by the Si_{As} defect. The reduction of the activation energy to only 60 meV indicates to us that a substantial lattice relaxation has taken place but we cannot be more specific as to the amount of this localized distortion.

The 43-meV activation energy observed for trapping at a vacancy-impurity complex is disappointingly noninformative since we do not know the nature of the impurity. Currently, we are restricted simply to noting that an activation energy is observed in the case of this defect and that the lattice distortion is substantial around the complex.

We will conclude this section of the discussion by considering the lifetime data in the temperature ranges in which only one lifetime component could be resolved in undoped GaAs and Si-doped samples. For undoped GaAs the lifetime has a value of 233 ps for unannealed samples and 225 ps for annealed samples. For Si-doped samples the corresponding lifetime values are 230 and 225 ps. These lifetimes are all somewhat larger than the bulk lifetime (220 ps as deduced from the Cd-doped samples) and show, therefore, that we are not observing annihilation from the bulk state only. The fact that the lifetimes are larger than the bulk lifetime suggests that some trapping is occurring at defects, but only to such a small extent that separation into two distinct lifetimes is not possible; i.e., the trapping rate κ into these defects is so small that the observed lifetime τ_1 [$=(\lambda_B+\kappa)^{-1}$; see Eq. (1)] is close to the lifetime of trapped positrons. Note that at higher temperatures the trapping rate has increased sufficiently so that the value of τ_1 becomes sufficiently small to permit a separation into two lifetime components. It is only because of this reduction in the observed lifetime for positrons in the bulk state that it is possible to separate the 225-ps lifetime as a lifetime measurably different from the bulk-state lifetime component.

C. Light-irradiation effects

These measurements have not been made extensively and thus only serve to demonstrate that light irradiation can indeed have an effect on positron annihilation although here only in the case of undoped and unannealed GaAs. According to Table I, ΔI_2 increased with light intensity (at 45 K) and the lifetime is close to the value obtained without light irradiation but at higher temperatures. This simply indicates that the defects have been activated, probably by trapping of electrons liberated from the valence band. As the temperature is increased I_2 decreases to zero at 150 K, indicating that an increased amount of recombination with holes takes place, thus reducing the number of electrons trapped by the defect to zero. The absence of a light-induced effect in Si- and Cd-doped samples suggests that the impurities present are

either electron traps (but not positron traps) or recombination centers. Further experiments are certainly in order to unravel the potential of this method, but we believe that this method should, in fact, provide information on the much sought correlation between energy levels and the physical nature of the defect.

V. CONCLUSIONS

In this paper positron-annihilation lifetimes have been investigated in grown-in defects in GaAs. The main body of the investigations fell into two parts: isochronal-annealing data in the 20—750 °C temperature range with measurements performed at room temperature, and at-temperature measurements in the range 20—300 K using samples subjected to various amounts of isochronal annealing.

A careful examination of the present data as well as older data using the same batch of samples has revealed the following.

(1) The bulk lifetime for GaAs is about 200 ps, as observed directly in Cd-doped GaAs (*p*-type material).

(2) Vacancy-impurity pairs (when present) yield a lifetime of 290 ps, which is indicative of a monovacancy. No evidence for divacancies was found regardless of annealing or measuring temperature. Silicon occupying an arsenic position is a positron trap giving a lifetime of about 260 ps.

(3) High-temperature annealing appears to create Ga_{As} antisite defects. No evidence for V_{As} could be detected. It is proposed that during high-temperature annealing V_{As} is converted into a Ga_{As} and V_{Ga} pair, the latter being lost to sinks. The positron lifetime for the Ga_{As} defect is about 225 ps and thus very close to bulk lifetime.

(4) At low temperatures the defects are rendered inaccessible to positrons. The temperature region in which this happens depends on the defect in question. The shorter the lifetime, the higher the temperature regime in which the trapping rate changes. Several models for this phenomenon were considered, keeping in mind the case of silicon where the opposite effect has been observed, i.e., the trapping rate decreases with increasing temperature. It is suggested that the reason for the reduction in trapping rate is due to an energy barrier arising predominantly from the localization of the positron wave function around As atoms (anions), but modified according to the detailed configuration of atoms surrounding the defect in question.

(5) Light irradiation has been shown to activate defects at low temperatures. The effect was only present in undoped GaAs and ceased to exist at temperatures higher than ~ 160 K.

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