Detection of vacancy-like defects during Cu diffusion in GaAs by positron annihilation

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Abstract. The positron annihilation spectroscopy is a method for direct characterization of vacancy-type defects by measuring the positron lifetime. It provides information about open volume and concentration of defects. Such measurements were carried out to study the defect properties of semi-insulating GaAs after copper diffusion. A 30 nm layer of Cu was deposited by evaporation to undoped GaAs samples. The diffusion of Cu was performed during an annealing step at 1100 °C under different arsenic vapor pressures. The samples were quenched into room temperature water. The initial semi-insulating (SI) undoped GaAs sample shows no positron traps in that state. After gentle annealing, a vacancy-type defect complex in addition to shallow positron traps was observed to be an efficient positron trap. After Cu in-diffusion during the annealing process, the shallow positron trap is believed to be the CuGa double acceptor. The exact nature of the vacancy-like defects could not be determined unambiguously. The concentration of these defects exhibits inverse relationship to the arsenic vapor pressure. Thus, the arsenic vacancy is believed to be part of this complex. The temperature-dependent Hall-effect measurements have revealed the presence of an acceptor level at $E_V + 0.5$ eV that is usually attributed to CuGa.

1. Introduction
Despite extensive studies on GaAs during the recent decades, we do not yet have a full understanding of native point defects in this material. The thermodynamic properties of these defects in GaAs are of great technological interest. The thermodynamic analysis helps predicting the concentrations of the point defects incorporated into crystal under equilibrium conditions [1, 2]. The subject of the present work is the investigation of point defects quenched from different equilibrium states by means of positron annihilation lifetime spectroscopy (PALS). The positron has proved to be a valuable nondestructive probe for vacancy-type defects. During the past decades, PAL has been intensively applied to characterize defects in various semiconductors [3]. But in many cases it is difficult to conclude from the annihilation parameters alone which defect is responsible for the positron trapping. Basic thermodynamic considerations displayed in this paper helped us a lot in characterizing the origin of the observed vacancy-complex. The native point defect concentration can be expressed as a function of temperature and arsenic vapor pressure according to the law of mass action [1].

Copper is found as an unintentional impurity in most semiconductors. This is owing to the fact that Cu is a rapidly diffusing contaminant already at low temperatures. Cu exhibits an unusually large

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diffusion coefficient in many semiconductor crystals. In GaAs, it was found to be as high as \( D = 1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) at 500 °C and \( D = 1.8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \) at 100 °C \[4\]. Cu diffuses very fast by interstitial diffusion (kick-out process) \[5\]. Figure 1 presents the experimentally obtained solubility of Cu as a function of temperature as reported in Ref. 4. Moreover, the solubility was calculated to be \( 5 \times 10^{9} \text{ cm}^{-3} \) at 100 °C \[4\]. Depending on the cooling speed after a diffusion process, only a small fraction of the total Cu concentration is electrically active as acceptors. The portion of Cu that remains electrically inactive forms Cu-Ga precipitates \[6\].

![Figure 1. Solubility of Cu in undoped GaAs as a function of temperature (Ref. 4).](image)

### 2. Experimental

The investigated samples were cut from the semi-insulating undoped LEC grown GaAs wafer (\( 5 \times 5 \times 0.5 \text{ mm}^3 \)). The resistivity of initial material was about \( 10^6 – 10^7 \Omega \text{ cm} \). The samples were covered by 30 nm Cu by evaporating it under UHV conditions. This amount of Cu corresponds to a volume concentration of \( 6 \times 10^{18} \text{ cm}^{-3} \) which is approximately the upper solubility limit of Cu in GaAs at 1100 °C \[4\]. The deposited layer thickness was controlled by a thickness measurement device (frequency shift of a crystal oscillator) which was calibrated before by Atomic Force Microscopy. High purity copper-free quartz ampoules HSQ300 (Heraeus Quarzglas GMBH&Co) were used for the Cu diffusion annealing. Pure As (99.999%) was used as an arsenic source. The samples and the arsenic source were sealed in quartz ampoules under high vacuum. Annealing was performed for three hours in a two-zone temperature furnace at 1100 °C (sample temperature). The temperature of the arsenic source was varied in the region of 550 – 740 °C, which corresponds to an As-pressure of 0.2 – 9.68 bar \[7\]. After annealing, the ampoules were quenched into water at room temperature. According to the solubility, Cu is in oversaturated state and Cu atoms have the tendency to leave the lattice and start the out-diffusion, e.g. by forming precipitates. Hall-effect measurements were applied to measure the samples in the as-quenched state. Thereafter, the samples were isochronally annealed in the temperature range up to 850 K. The samples were cooled down relatively slowly after each annealing step. Between the annealing steps, PALS measurements in the temperature range of 20 – 500 K were carried out using a conventional fast-fast coincidence system with a time resolution of 225 ps. The
\(^{22}\)Na positron source was sandwiched between two identical 1.5 µm thick Al foils and placed between two identical samples. The spectra were analyzed with the two-component trapping model (one defect type) after source and background correction. The annealed SI GaAs samples were investigated by temperature-dependent Hall-effect measurements (T = 293…373 K). The samples annealed at 0.2 and 9.68 bar of As vapor pressure were chosen for chemical analysis by titration measurements.

3. Result and Discussion
The semi-insulating undoped GaAs sample without any Cu deposition (reference sample) did not show any positron trapping. After Cu in-diffusion, the average lifetime increases only slightly in the high-temperature region, which indicates detection of a small number of vacancy-type defects. Figure 2 represents the average positron lifetime versus measurement temperature after different annealing steps performed after Cu in-diffusion. A distinct decrease of the average lifetime at low temperatures is clearly shown for all curves. This is a typical dependence for shallow positron traps (negatively charged, non-open volume defects, such as ionized acceptors), which tend to trap positrons in the extended region of the Coloumbic potential, reflecting thereby the properties of the bulk as the annihilation characteristics of the positrons [3, 8]. Shallow traps are effective only at low temperatures due to the small binding energy of positron, while at higher temperatures positrons are detrapped because of the high detrapping rate. Here, after Cu in-diffusion, the shallow traps must be ionized Cu acceptor. Their concentration is up to \(3 \times 10^{17} \text{ cm}^{-3}\) according to the Hall-effect measurements. During annealing up to 750 K, the average positron lifetime increases strongly up to the value of 260 ps, indicating the presence of vacancy-type defects. With a further increase of the annealing temperature, a rapid decrease of the average positron lifetime was observed. With annealing at temperatures higher than 800 K the vacancy clusters grow and the distance between them becomes larger than the positron diffusion length. Thus, they become invisible for positrons [9].

![Graph](image.png)

**Figure 2.** Average positron lifetime as a function of sample temperature in undoped SI GaAs. Prior to the experiment, about \(6 \times 10^{18} \) Cu atoms were introduced by evaporating a layer of 30 nm Cu onto the sample surface and by subsequent annealing at 1100 °C under 5.57 bar of As pressure (3h, then quenched into water). The temperature-dependent lifetime experiment was carried out after each annealing step as illustrated in the figure.
Figure 3 shows the annealing behavior of the average and defect-related lifetimes and its intensity. It can be shown that the open volume of the detected vacancy-type defect increases during annealing. The defect-related lifetime increases with increasing the annealing temperature but lies in the monovacancy region until the annealing temperature 750 K. The defect-related lifetime reaches the value of 332 ps at 800K but with a low intensity, which corresponds to divacancies (upper panel of figure 4).

Figure 3. Positron lifetime results of the annealing experiment of undoped semi-insulating GaAs after in-diffusion of $6 \times 10^{18}$ cm$^{-3}$ Cu atoms at 1100 °C under 5.57 bar of As pressure. The average lifetime is shown in the upper panel. The defect-related lifetime and its intensity versus the annealing temperature are plotted in the lower two panels. The spectra were measured at a sample temperature of 466 K to diminish the influence of the shallow traps.

The lower panel of figure 4 represents the defect concentration versus the annealing temperature where the defect concentration increases from $6.97 \times 10^{16}$ cm$^{-3}$ at 550 K up to $1.49 \times 10^{17}$ cm$^{-3}$ at 750 K and decreases again at 800 K. The defect concentration is determined according to equation (1):

$$K_d = \frac{\mu C}{\tau_b} \left( \frac{\tau_{av} - \tau_b}{\tau_d - \tau_{av}} \right).$$

(1)

$K_d$ is the trapping rate, $\mu$ is the trapping coefficient and taken as $10^{15}$ s$^{-1}$ at 300 K [10,11], $\tau_b$ is the bulk lifetime 230 ps [12,13], $\tau_{av}$ is the average positron lifetime and $\tau_d$ is the defect-related lifetime. The upper panel in figure 4 represents the number of vacancies versus the annealing temperature where the number of vacancies is one vacancy in the temperature range up to 750 K and increase to be 2 vacancies at 800 K. This was concluded according to the calculation in Ref. 14 which is based on the superimposed-atom model by Puska and Nieminen [15].

To show the effect of Cu, we would like to compare the results above to the sample which was not treated with Cu and annealed under very similar conditions. As shown in figure 5, the as-quenched sample shows a higher value of the average lifetime. This can be attributed to the trapping of positrons in vacancies. The pronounced decrease of the average positron lifetime at temperatures below 200 K,
may be explained by positron trapping at negative ions (shallow traps), $C_{-}\text{As}$. Where semi-insulating high resistive crystals are produced by intentional doping of GaAs with carbon atoms, which are incorporated exclusively on the As sublattice forming shallow acceptor-like defects, $C_{\text{As}}$ [1]. But this cannot be identified from the results of positron lifetime alone. With increasing the annealing temperature the average lifetime decreases. This is owing to the fact that the vacancies disappear. In contrast, in the case of GaAs samples after Cu in-diffusion (figure 2), almost no change of the average positron lifetime was observed in the as-quenched state. However, during the annealing steps until 750 K the average positron lifetime increases strongly, and at annealing temperatures higher than 800 K the vacancy cluster signal almost disappears.

**Figure 4.** Defect concentration and the number of vacancies as a function of the annealing temperature in undoped SI GaAs after in-diffusion of $6\times10^{18}$ cm$^{-3}$ Cu atoms at 1100 °C under 5.57 bar of As pressure. The number of vacancies in the observed clusters is shown in the upper panel. The defect concentration versus the annealing temperature is plotted in the lower panel. These Data were calculated using the positron lifetime results presented in figure 3.

Figure 6 shows the temperature dependence of the average and defect-related lifetime on the sample temperature for undoped semi-insulating GaAs annealed at 1100 °C for 3 hours under different arsenic vapor pressures compared with an unannealed reference sample. No Cu was incorporated into the samples. As shown in the lower part, no vacancy defects were observed in as-grown semi-insulating GaAs. The average positron lifetime of the reference sample is close to the defect-free bulk value of 230 ps at all measurement temperatures. After annealing, the average positron lifetime is strongly enhanced, which indicates the generation of vacancy-like defects during the annealing treatment.

The decrease of the average positron lifetime at low temperatures is due to positron trapping at shallow positron traps. With increasing the arsenic vapor pressure during annealing, the average positron lifetime decreases. The maximum average lifetime is observed after annealing at 0.2 bar. Since the average positron lifetime determines the magnitude of the positron trapping rate and thus the
concentration of the vacancy-like defects, the pressure dependence of \( \tau_{av} \) reflects an inverse relation between the concentration of the vacancy defects at 1100 °C and the arsenic vapor pressure. The upper part in figure 6 presents the defect-related lifetime obtained from the two-component decomposition of the spectra as a function of the measurement temperature. The defect-related lifetime for all the samples at 300 K is 293±10 ps, which is distinctly higher than the lifetimes in Te- and Si-doped GaAs (254 and 262 ps respectively) where Ga vacancies were found to be responsible for the positron trapping. But this value still lies in the region for a monovacancy, because the value calculated for the \( V_{Ga}^{-}V_{As}^{+} \) divacancy defect in GaAs is 332 ps [16]. Since the defect-related lifetime for As vacancies in GaAs is about 290-300 ps [17], then based on the measured defect-related lifetime the observed vacancy-like defects attributed to As vacancies. In addition, this is found to be in a good agreement with the thermodynamic considerations.

Let us consider the basic thermodynamic reactions for the vacancy formation in GaAs as:

\[
\frac{1}{4} As_4^{gas} \leftrightarrow As_{As} + V_{Ga}.
\] (2)

for the Ga vacancy and

\[
As_{As} \leftrightarrow V_{As} + \frac{1}{4} As_4^{gas}.
\] (3)

for the As vacancy. The arsenic tetramer was chosen because it is the dominating As vapor component [18]. Thus, the concentrations of the Ga and As vacancies at a certain temperature should depend on the arsenic vapor pressure. According to the mass action law, the concentrations of these defects can be derived as:

\[
[V_{Ga}] = K_{VGa} \times P_{As}^{1/4},
\] (4)

\[
[V_{As}] = K_{VAs} \times P_{As}^{1/4}.
\] (5)

where \( K_{VGa} \) and \( K_{VAs} \) are mass action constants for gallium and arsenic vacancies at a certain temperature and \( P_{As} \) is the ambient arsenic vapor pressure. From equations (4) and (5), it is clear that the concentrations of \( V_{Ga} \) and \( V_{As} \) should have an opposite behavior with respect to As vapor pressure and the \( V_{As} \) concentration is inversely proportional to the arsenic vapor pressure, which gives us the possibility to discriminate between these two vacancies in both sublattices.

Figure 5. Average positron lifetime as a function of sample temperature in undoped SI GaAs. The samples were annealed at 1100 °C under 5.57 bar of As pressure. The samples were not treated with copper as a reference experiment to the results shown in figure 3. The temperature-dependent lifetime experiment was carried out after each annealing step as illustrated in the figure.
Figure 6. Average and defect-related positron lifetime versus measurement temperature for undoped semi-insulating GaAs annealed at 1100 °C for 3 hours under different arsenic pressures compared to a not annealed reference sample. Lines are to guide the eye only.

Figure 7 reveals an opposite behavior of the concentrations of the vacancy-like defects with increasing $P_{\text{As}}$ compared to the data for $n$-type Si-doped GaAs ($[\text{Si}] = 2 \times 10^{19} \text{ cm}^{-3}$) [19]. The two-component trapping model and the specific trapping coefficient of $10^{15} \text{ s}^{-1}$ at 300 K were used for calculating the vacancy concentrations. The fits to the experimental data (solid lines in figure 7) represent the power law and yield an exponent close to 0.25 for GaAs:Si and $-0.25$ for SI GaAs. As shown, for the GaAs:Si the vacancy concentration increases with increasing arsenic pressure, which refers to the Ga vacancy and is in accordance with the well-known formation of the $V_{\text{Ga}}$-Si$_{\text{Ga}}$ defect complex in this material [11]. The same pressure dependence was also found in Te-doped GaAs [20]. The vacancy concentration in SI GaAs exhibits an opposite behavior and decreases with increasing arsenic pressures, which is characteristic for the $V_{\text{As}}$. Based on these results, the origin of observed vacancy-like defects in annealed semi-insulating GaAs is ascribed to $V_{\text{As}}$. On the other hand, it cannot be the isolated As vacancy. Arsenic vacancies should be positive (and thus not detectable with positrons) in semi-insulating or in $p$-type GaAs, where the position of Fermi level is in the middle or in the lower part of the band gap. The Hall-effect measurements showed that all investigated annealed samples became slightly $p$-type with a concentration of $[p] = 10^{11}$-$10^{12} \text{ cm}^{-3}$ that corresponds to the position of Fermi level at 0.4-0.5 eV above the valence band. Also all theoretical calculations agree that the arsenic vacancy is always positive in SI or at least in $p$-type GaAs and thus it should be invisible for positrons [3]. This leads us to suppose that we are dealing with a $V_{\text{As}}$ defect complex which is not any more positively charged. Since Cu is the most common impurity in annealing studies [6, 21, 22], Cu is the first candidate that can be responsible for the formation of such a complex.

The concentration of the Cu impurities for the two samples annealed at 0.2 and 9.68 bar was determined by titration measurements (full magenta circles in figure 7). As can be seen, the Cu concentration was about $10^{10} \text{ cm}^{-3}$ only; that is one order of magnitude lower than the measured number of the vacancy-complex. This means that copper is not a constituent of the observed defect complex. The observed $V_{\text{As}}$-like defect should be related to a native defect-complex. The exact nature of this complex cannot be determined from the results of positron annihilation alone. More likely, the
electrically active part of Cu impurities acts as shallow positron traps. It causes the decrease of average positron lifetime in the low temperature region. Indeed, the temperature-dependent Hall-effect measurements have revealed the presence of an acceptor level at $E_V + 0.5$ eV that is usually attributed to CuGa related defects [21, 22].

![Figure 7. Vacancy defect concentrations in semi-insulating and Si-doped GaAs versus As vapor pressure during annealing at 1100 °C (Ref. 18). Solid lines are the power law fits to the data points. Closed circles present the concentration of Cu impurities obtained with the help of titration measurements for the samples annealed at 0.2 and 9.68 bar.]

4. Summary

Positron annihilation lifetime was used to investigate the formation of point defects in undoped semi-insulating GaAs during the diffusion of copper. Our experiment findings are summarized below:

Almost no positron trapping is found after quenching from diffusion temperature (1100 °C), when Cu is distributed all over the crystal, i.e. after in-diffusion. During a subsequent annealing up to 750 K after the diffusion treatment (out-diffusion), the average positron lifetime increases strongly indicating the detection of vacancy-type defects. With a further increase of the annealing temperature to 850 K, a rapid decrease of the average positron lifetime was observed. It is probably due to the fact that vacancy clusters grow and the distance between them becomes larger than the positron diffusion length. Another possible reason for the disappearance of the vacancy signal is that vacancy clusters are dissolved. This cannot be distinguished by the obtained data alone.

It can be shown from the annealing behavior of the average lifetime that the open volume of the detected vacancy-like defect increases during annealing, in contrast to the semi-insulating undoped GaAs samples annealed under very similar conditions but not treated with Cu. The average lifetime decreases with increasing the annealing temperature. The defect concentration increases with increasing the annealing temperature up to 750 K. The number of vacancies incorporated in the observed clusters is one vacancy in the annealing temperature range up to 750 K and increases to reach 2 vacancies at 800 K. Vacancy-like defects and shallow positron traps were observed.

On the basis of positron annihilation parameters and thermodynamic considerations, it was concluded that the observed vacancy-like defect contains an arsenic monovacancy. The results obtained at undoped SI GaAs were compared to the results of similar experiments done on n-type Si-doped GaAs to confirm the reliability of such thermodynamic considerations, where the existence of a donor-gallium vacancy complex is well known.
The difference of the arsenic vapor pressure dependence of the vacancy concentration for undoped SI and n-type Si-doped GaAs was clearly shown. Taking into account that the isolated $V_{As}$ in a $p$-type sample is positive and accordingly invisible to positrons, the presence of a vacancy complex containing an As vacancy was assumed. The charge of this complex must be neutral or negative in our $p$-type samples. Due to the high solubility and high diffusion coefficient of copper in GaAs, it was the first candidate that could be responsible for this complex. The contamination of Cu atoms was confirmed with means of titration measurements but the concentration was almost one order of magnitude lower than the vacancy concentration that is calculated from positron lifetime measurements.

We believe that the observed vacancy complex is not bound to Cu impurities and represents a native defect complex. But the structure of the complex cannot be exactly determined from positron annihilation parameters alone. The observed shallow traps in Cu-diffused GaAs can be explained by copper contamination. Cu atom placed on a Ga sublattice forms a double acceptor Cu$_{Ga}$\(^{2+}\) (energy level $E_F + 0.5$ eV) that acts as a positron shallow trap. The temperature-dependence Hall-effect measurements confirmed the existence of this acceptor level. But in SI GaAs samples which were not treated with Cu, shallow positron traps could be explained by negative ions, $C_{As}^{-}$.

Acknowledgments

We would like to thank B. Gruendig-Wendrock (TU Bergakademie Freiberg) for performing Hall measurements and S. Eichler (Freiberger Compound Materials GmbH) for providing the samples materials.

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