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Published in:
Journal of Applied Physics

DOI:
10.1063/1.366703

Published: 01/01/1998

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
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Citation: Journal of Applied Physics 83, 71 (1998); doi: 10.1063/1.366703
View online: http://dx.doi.org/10.1063/1.366703
View Table of Contents: http://aip.scitation.org/toc/jap/83/1
Published by the American Institute of Physics
Study of defects in electron irradiated CuInSe$_2$ by positron lifetime spectroscopy

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(Received 7 July 1997; accepted for publication 26 September 1997)

CuInSe$_2$ was studied in the as-grown state and after low-temperature (4 K) 2 MeV electron irradiation. The positron bulk lifetime of 235 ps was measured for the unirradiated sample. The positron bulk lifetime was theoretically calculated and is in good agreement with the experimental value. In addition, the defect-related lifetimes for mono-, di-, and trivacancies are theoretically determined. An increased average positron lifetime indicated after electron irradiation the appearance of open-volume defects, most probably of divacancy type. The disappearance of this defect was observed during annealing below 250 K. Other defects were formed leading to a divacancy signal at least stable up to 600 K in the temperature range above 450 K. © 1998 American Institute of Physics.

I. INTRODUCTION

The ternary I–III–VI$_2$ compounds, such as CuInSe$_2$ (CIS), crystallize in the chalcopyrite structure. CIS-based layers are used as very high-efficient adsorbers for thin-film solar cells. The best conversion efficiency experimentally obtained is 17%. A further important advantage of this material is the high radiation resistance.

Point defects influence electrical and optical properties of CIS. Native defects partly compensate deviations from the ideal stoichiometry. Some of them introduce energy levels in the band gap and, therefore, the conductivity type can be adjusted by appropriate compositions of the compound. A difficulty is the large number of intrinsic defects in ternary compounds. Calculations of the defect chemistry of this compound, and also of other $A_{x}B_{y}X_{z}$ compounds, are, in principle, possible. The applied model allows, in principle, the calculation of the concentration of all 12 intrinsic defects as a function of the composition and temperature. In addition, the concentration of the defects in their different charge states and the electron and hole concentrations can be obtained. The results of these calculations are described in detail in Sec. V.

Irradiation-induced defects play an important role in the degradation of thin-film solar cells in space. The underlying damage formation mechanisms were reviewed for several solar cell materials by Woodyard.

The positron annihilation spectroscopy, a well-established method to study vacancylike defects in solids, can yield valuable information on the structure of vacancies. Positrons may be trapped in open-volume defects and change their annihilation parameters specifically. Because of their charge, positrons are sensitive to different charge states of a vacancy in semiconductors, and thus, they represent a selective tool for their identification. First applications of positron annihilation to the investigation of open-volume defects in CIS were recently published. These results were obtained in epitaxially grown layers by the slow positron beam technique and are, thus, not directly comparable to the presented positron lifetime measurements in bulk material. To the best of our knowledge, there exist no further positron lifetime values in the literature up to now.

Monovacancies, or at most divacancies, can be produced by irradiation with 0.5–3 MeV electrons in crystals. This treatment was applied to CuInSe$_2$, and the formation and annealing behavior of vacancylike defects was investigated. Additionally to vacancies, electron irradiation produces, for example, negative ions (negatively charged nonopen volume defects) in crystals. These negative ions act as shallow traps for positrons in semiconductors.

In the following section, we summarize the material and experimental details. Section III gives a short introduction to the method of positron lifetime spectroscopy and its specific features used to study vacancy defects in semiconductors. In Secs. IV and V, we describe the results of calculations of positron lifetimes in bulk material and in defects and the defect chemistry in CuInSe$_2$. In Sec. VI, the results obtained by positron annihilation in as-grown and irradiated CuInSe$_2$ will be presented and also discussed. Conclusions are drawn in Sec. VII.

II. MATERIAL AND EXPERIMENTAL PROCEDURES

Bulk crystals of CuInSe$_2$ were grown by the Bridgman method. The samples of this material available to us were first studied by positron lifetime spectroscopy. Different re-
results were obtained, i.e., there were samples showing different average positron lifetimes in dependence on their compositions. However, these interesting results are not the subject of this paper. We rather chose a sample exhibiting a single component spectrum with the lowest average positron lifetime measured, i.e., showing no positron trapping (see discussion in Sec. VI A). From this result, we concluded that no lattice defects were detectable in this sample by positrons. We favored this sample for the electron irradiation experiment, since the absence of detectable defects prior to the irradiation allows the almost undisturbed study of irradiation-induced defects.

The Cu/In/Se composition of this sample was determined by microprobe measurements to be 0.3/0.18/0.52 after completion of irradiation and annealing experiments. This is a relatively large deviation from the stoichiometric point leading to the occurrence of at least one second phase. This is a typical problem of those ternary compounds. The positron source is large compared to the dimensions of second-phase inclusions. Hence, the measured positron lifetime is an average value of the lifetimes of the different phases. It is composed from the defect-related lifetimes in the occurring phases weighted by their corresponding volume fractions. Since the CuInSe$_2$ phase dominates, we assume that the detected irradiation-induced defects are typical for this phase.

Electron irradiation was performed at 4 K with a Van der Graaff accelerator in the Forschungszentrum Jülich. The incident energy of electrons was 2 MeV, and a fluence of $10^{18}$ cm$^{-2}$ was applied for irradiation. The irradiated samples were mounted under liquid nitrogen in a cryoheater system to prevent warming up and annealing. Thereafter, an isochronal annealing (15 min) was performed in the range between 90 and 580 K. Temperature-dependent measurements after different annealing steps were carried out starting at 15 K.

The positron lifetimes were measured by using a fast-fast coincidence system having a time resolution of 260 ps. A pair of identical samples (two halves of the original sample) was sandwiched with the positron source consisting of radioactive $^{22}$NaCl (0.5 MBq) covered with two thin (1 mg/cm$^2$) Al foils. The lifetime spectra consisting of about $5 \times 10^6$ annihilation events were analyzed after source and background corrections$^{11,12}$ with the trapping model$^{13,14}$

Hall-effect measurements were performed according to Van der Pauw.$^{15}$ The sample under investigation was found to be in the $p$-type conductivity state prior and after irradiation. Thus, the Fermi level was located close to or within the valence band.

III. POSITRON TRAPPING IN DEFECTS

Positrons are obtained by the $\beta^+$ decay of $^{22}$Na. Their lifetime can be determined by detecting the time difference between the birth gamma (1.27 MeV gamma of $\beta^+$ decay) and the annihilation gamma (0.51 MeV). The lifetime spectrum consists of a sum of exponential decay components with the lifetimes $\tau_i$ and their intensities $I_i$. Positrons annihilate from the delocalized ground state in a perfect crystal. A single positron lifetime will be measured, $\tau = \tau_b$ (b: bulk). In the presence of defects of a distinct type, positrons may get localized at them and annihilate with a second lifetime $\tau_2 = \tau_d$ ($d$: defect). This lifetime is larger than $\tau_b$ for open-volume defects, such as vacancies, due to the decrease in the electron density of the defect compared to the bulk. The lifetime spectrum consists, then, of two components. The positron trapping rate at defects, $\kappa$, may be determined from the experimentally obtained average positron lifetime $\bar{\tau} = I_1 \tau_1 + I_2 \tau_2$ (with $\tau_2 = \tau_d$) according to Eq. (1). The positron trapping rate $\kappa$ is proportional to the defect concentration $C_d$. The proportional constant $\mu$ is the trapping coefficient, and must be obtained at least once by an independent reference method,

$$C_d = \frac{\kappa}{\mu \cdot \tau_b} \frac{\tau - \tau_b}{\tau_d - \tau}.$$  

(1)

Semiconductor defects can exist in different charge states, depending on the position of the Fermi level in the energy band gap. A negative or positive charge state gives rise to additional Coulomb tails of the potential. Hence, positively charged vacancies are repulsive for positrons. The positron trapping in neutral vacancy defects is distinct, and moreover, the trapping is strongly enhanced in negative vacancies at low temperatures. The positron trapping at neutral vacancies is assumed to be temperature independent. The trapping coefficient $\mu$ depends on the defect type, defect charge, and possibly on temperature. Values for negative vacancies are $\mu = 1 \times 10^{15}$ s$^{-1}$ at 300 K (Refs. 16 and 17) and $\mu = 10^{16} - 10^{17}$ s$^{-1}$ at 20 K. $^{17,18}$ $\mu$ is assumed to be about $10^{14} - 10^{15}$ s$^{-1}$ for neutral vacancies.$^{19}$

Additionally, so-called shallow positron traps are possible candidates for positron trapping. They are negatively charged non-open-volume defects (negative ions), which are able to localize positrons in extended Rydberg states at low temperatures.$^{8,10}$ The positron lifetime in shallow traps is close to that in the bulk due to the negligible changes of the electron density felt by the positron. Therefore, as a result of competition between positron trapping in vacancies and in shallow traps, only the temperature dependence of the positron lifetime proves the presence of these shallow positron traps. The decomposition of the spectra is specially difficult at low temperatures due to this competitive trapping centers.

This temperature dependence of trapping in extended Rydberg states can be described$^{20}$ by

$$\kappa_{st} = \kappa_{st0} T^{-1/2} = \mu_{st0} \frac{C_{st}}{N} T^{-1/2}.$$  

(2)

$N$ is the number of atoms per cm$^3$, $C_{st}$ (st: shallow trap) corresponds to the defect concentration, and $\mu_{st0}$ and $\kappa_{st0}$ are the trapping coefficient and trapping rate, respectively, at 20 K. The trapping coefficient of negative ions in electron irradiated GaAs was determined to be $(5 \pm 2) \times 10^{10}(T/K)^{-1/2}$ s$^{-1}$. $^{21}$ To simplify the model, only one effective Rydberg state was supposed instead of the complete Rydberg series.

The thermal detrapping from the shallow potential becomes dominant at higher temperatures, i.e., above 300 K, and almost no significant influence on the positron trapping is detectable. The temperature dependence of the detrapping rate $\delta$ from Rydberg states is given by
\[
\delta = \frac{\mu_{\text{opt}}}{N} \left( \frac{m^* k_B T}{2 \pi \hbar^2} \right)^{3/2} e^{-E_b/\hbar k_B T}.
\]

\(E_b\) is the binding energy of positrons to the shallow trap, \(k_B\) the Boltzmann constant, and \(m^*\) the positron effective mass.

It should be noted that it is hardly possible to distinguish an isolated vacancy from a larger complex containing a vacancy by means of positron annihilation. Therefore, we cannot exclude that a detected vacancy is part of a defect complex.

**IV. THEORETICAL CALCULATIONS OF POSITRON LIFETIMES**

We used the superimposed-atom model by Puska and Nieminen\textsuperscript{22} to calculate the positron lifetimes in the perfect lattice as well as in different defects in CuInSe\(_2\). The calculations are described in detail elsewhere.\textsuperscript{23} CuInSe\(_2\) crystalizes in the chalcopyrite system. The copper and indium atoms occupy the corners and faces of the unit cell of this modified zinc-blende structure, while the selenium atoms replace the sulfur atoms in the zinc-blende structure. The number of unit cells (in defect calculations) and grid points was increased until the calculated lifetimes did not change anymore; by this we exclude the effects of the finite supercell size and of the discretization necessary for the numerical calculations, respectively.

We took for the calculations the low-frequency value \(\epsilon_0\) as well as an estimated value due to the lack of data on the high-frequency dielectric constant \(\epsilon_\infty\) (lowering the high-frequency dielectric constant analogously to the known ratio for GaAs, CdTe,...) and one of even lower and higher value. This is to demonstrate that the deviations are systematically due to a change in \(\epsilon\). Larger dielectric constants are known to decrease the calculated lifetime values.\textsuperscript{23}

The lifetimes calculated with the superimposed-atom model are always 5–7 ps lower than the corresponding experimental results.\textsuperscript{20} Here, we find the experimental bulk lifetime in the same range in comparison to the theoretical data when using the estimated value for \(\epsilon_\infty = 11.0\). The theoretical data can, thus, be scaled to the experimental bulk value as shown in the last column in Table I.

We have considered several types of vacancies in the lattice. The results are given in Table I. The lattice relaxation around the defects is not taken into account (see the discussion in Ref. 23). Note that the presented results are obtained with a non-self-consistent calculation method (see Ref. 23 for a discussion of the differences in self-consistent and non-self-consistent calculations).

As we can see from Table I, the lifetimes for different monovacancies are very close to each other, so that experimentally no distinction will be possible with a lifetime spectrometer. This is reflected in the very similar contour plots of the position probability density of the positron. Hence, we show only one example, the In vacancy. Here, we can see that, in comparison to the bulk, the positron wave function is localized at the site of the vacancy.

The calculated lifetimes are very close to each other (see Table I) for \(V_{\text{CuSe}}\) and \(V_{\text{InSe}}\), considering all three possible combinations of nearest-neighbor divacancies. Thus, the calculated lifetimes were scaled to the experimentally determined bulk value \(\tau_0 = 235\) ps (last column) using the best estimate for \(\epsilon_\infty = 11.0\). The scaling is to provide a better comparability to the experimental data. The lifetimes for monovacancies are very similar, indicating nearly the same electron densities where the positron is localized. Concerning the divacancies, the CuIn divacancy leads to a lower lifetime since the missing atoms are closer together.

<table>
<thead>
<tr>
<th>(\tau (\text{ps}))</th>
<th>(\epsilon = 6.0)</th>
<th>(\epsilon = \epsilon_\infty = 13.6)</th>
<th>(\epsilon = 20)</th>
<th>(\epsilon = \epsilon_\infty = 11.0)</th>
<th>(\epsilon = \epsilon_\infty = 11.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>235</td>
<td>226</td>
<td>224</td>
<td>228</td>
<td>235</td>
</tr>
<tr>
<td>(V_{\text{Cu}})</td>
<td>251</td>
<td>241</td>
<td>238</td>
<td>243</td>
<td>250</td>
</tr>
<tr>
<td>(V_{\text{In}})</td>
<td>258</td>
<td>247</td>
<td>244</td>
<td>249</td>
<td>257</td>
</tr>
<tr>
<td>(V_{\text{Se}})</td>
<td>254</td>
<td>243</td>
<td>241</td>
<td>245</td>
<td>253</td>
</tr>
<tr>
<td>(V_{\text{CuIn}})</td>
<td>275</td>
<td>262</td>
<td>259</td>
<td>264</td>
<td>272</td>
</tr>
<tr>
<td>(V_{\text{CuSe}})</td>
<td>304</td>
<td>289</td>
<td>285</td>
<td>292</td>
<td>301</td>
</tr>
<tr>
<td>(V_{\text{InSe}})</td>
<td>310</td>
<td>295</td>
<td>291</td>
<td>298</td>
<td>307</td>
</tr>
<tr>
<td>(V_{\text{CuInSe}})</td>
<td>342</td>
<td>323</td>
<td>319</td>
<td>326</td>
<td>336</td>
</tr>
</tbody>
</table>

\textbf{TABLE I.} Calculated positron lifetimes in the bulk and in vacancy defects of CuInSe\(_2\). We used different values for the dielectric constant to demonstrate the change of the lifetimes since the exact high-frequency value is not known. The best estimate for \(\epsilon_\infty = 11.0\) is given. The charge of the vacancies was not considered in the theoretical calculations. The calculated lifetimes were scaled to the experimentally determined bulk value \(\tau_0 = 235\) ps (last column) using the best estimate for \(\epsilon_\infty = 11.0\). The scaling is to provide a better comparability to the experimental data. The lifetimes for monovacancies are very similar, indicating nearly the same electron densities where the positron is localized. Concerning the divacancies, the CuIn divacancy leads to a lower lifetime since the missing atoms are closer together.

![FIG. 1. Positron position probability density in the ideal lattice (a), in the In monovacancy (b), in the CuIn (c), and in the InSe divacancy (d) in CuInSe\(_2\). The symbols mark the atomic positions in the 110 plane. The contour spacing is 1/10 of the maximum value for (a), 1/12 for (b), and 1/20 for (c) and (d).]
TABLE II. Calculated formation enthalpies (in eV) of intrinsic defects in CuInSe$_2$. A formation entropy $\Delta S = 3k_B$ was assumed for all defects.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$V_{Cu}^{\alpha^+}$</th>
<th>$V_{In}^{\alpha^+}$</th>
<th>$V_{Se}^{\alpha^+}$</th>
<th>$Cu_{In}^{\alpha^+}$</th>
<th>$In_{Cu}^{\alpha^+}$</th>
<th>$Se_{Cu}^{\alpha^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation enthalpy$^a$</td>
<td>3.2</td>
<td>2.4</td>
<td>2.6</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Formation enthalpy$^b$</td>
<td>2.6</td>
<td>2.4</td>
<td>2.8</td>
<td>4.4</td>
<td>9.1</td>
<td>22.4</td>
</tr>
<tr>
<td>Defect</td>
<td>$Cu_{In}^{\alpha^+}$</td>
<td>$In_{Cu}^{\alpha^+}$</td>
<td>$Cu_{Se}^{\alpha^+}$</td>
<td>$In_{Se}^{\alpha^+}$</td>
<td>$Se_{Cu}^{\alpha^+}$</td>
<td>$Se_{In}^{\alpha^+}$</td>
</tr>
<tr>
<td>Formation enthalpy$^a$</td>
<td>1.9</td>
<td>1.6</td>
<td>5.4</td>
<td>5.0</td>
<td>6.0</td>
<td>5.2</td>
</tr>
<tr>
<td>Formation enthalpy$^b$</td>
<td>1.5</td>
<td>1.4</td>
<td>7.5</td>
<td>5.0</td>
<td>7.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

$^a$Reference 24.
$^b$Reference 25.
$^c$The value was printed incorrectly in Ref. 24.

V. DEFECT CHEMISTRY IN CIS

The concentration of the dominating defects can be estimated by means of defect chemistry. Some results are available for CuInSe$_2$ in thermodynamical equilibrium.$^{24,25}$ The usual approach to solve the problem is based on Kröger’s general ideas of the defect chemistry of ionic crystals. They give the theoretical background for these calculations on the basis of suitable thermodynamic variables such as the partial gas pressure or the thermodynamic activity of one of the components.$^{26-28}$ These ideas have been extended to ternary ionic compounds by Groenink and Jansse$^{29}$ under the assumption that anion–cation antisite defects can be neglected. These defects cannot be ruled out a priori in ternary semiconductors with mixed covalent and ionic bonding. Therefore, an extension of the model that allows the direct calculation of the concentrations of all intrinsic defects has been developed by one of the authors.$^3$ It requires the knowledge of the formation enthalpies and entropies, and the electronic levels of all 12 intrinsic defects.

Direct measurements of formation enthalpies and entropies of intrinsic defects of CIS have not yet been available because of the complexity of the defect chemistry. Therefore, one has to rely on indirect conclusions and theoretical estimates. Two approximate calculations of the formation energies of intrinsic defects have been carried out for CuInSe$_2$. The numerical results of the defect concentrations are presented as functions of the composition in a defect diagram, which shows the majority defects for a given range of compositions (Fig. 2).

Summarizing all results, one obtains that out of the 12 possible defects, only seven are relevant, the vacancies $V_{Cu}$, $V_{In}$, $V_{Se}$, the cation–cation antisites $Cu_{In}$, $In_{Cu}$ and the anion–cation antisites $Cu_{Se}$, $In_{Se}$. The remaining five defects, in particular, all interstitial defects, occur at concentrations that are orders of magnitudes lower compared to the dominant defect concentrations. Four different regimes for large deviations (>$1$ at. %) from the ideal stoichiometry have to be considered with the majority defects given in Fig. 2.

FIG. 2. Majority defects depicted in a ternary diagram of Cu, In, and Se for larger deviations from ideal stoichiometry. There are four regions characterized by the dominating defects: (1) $Cu_{Se}^+$, $Cu_{In}^+$, (2) $V_{Se}^{\alpha}$, $In_{Se}^+$, $Cu_{Se}^{\alpha+}$, (3) $In_{Cu}^{\alpha}$, $V_{Cu}^{\alpha}$, and (4) $Cu_{In}^+$, $V_{In}^{\alpha}$, $V_{Cu}^{\alpha}$. The composition range bounded by solid lines shows $n$-type conductivity.
were found at 50 and 80 meV (assigned to $V_{\text{In}}^{0/-}$) and at 50 and 100 meV ($Cu_{\text{In}}^{0/+}$). Donor-type defects were found at 60 and 80 meV ($V_{\text{Se}}^{0/-}$) and at 20 and 50 meV ($In_{\text{Cu}}^{0/-}$) below the conduction-band edge, respectively.

Since the sample is proved to be of $p$-type conductivity prior to and after electron irradiation, positron annihilation is restricted to the detection of Cu and In vacancies. It is known that negatively charged antisite defects may act as shallow positron traps at low temperatures. It can be concluded from Fig. 3 that $In_{\text{Se}}^{2/-}$, $Cu_{\text{In}}^{2/-}$, and $Cu_{\text{Se}}^{2/-}$ are possible candidates for these shallow traps in $p$-type material.

VI. RESULTS AND DISCUSSION

A. As-grown material

The composition of the investigated specimen (Cu 30 at. %, In 18 at. %, and Se 52 at. %) leads to $p$-type conductivity and belongs to region 1 in Fig. 2 with the majority defects $Cu_{\text{Se}}^{+/-}$ and $Cu_{\text{In}}^{+/-}$. It is expected that the concentration of any vacancy-type defect is orders of magnitudes lower than the concentration of these antisite defects. This is in agreement with the positron lifetime measurements of the as-grown sample, where an average positron lifetime of 235.2 ps has been measured. Since we have detected a one-component spectrum with the lowest lifetime ever observed in our $CuInSe_2$ samples, we conclude that this is the positron lifetime in bulk material. This means that the concentration of neutral and negatively charged vacancies is smaller than about $5 \times 10^{15}$ cm$^{-3}$.

The experimentally determined value is slightly higher in comparison with the calculated value of 228 ps (see Table I). This difference is typical for such a type of calculations using the superimposed-atom model and is also found in other semiconductors. This discrepancy between the calculated and experimentally determined positron lifetimes is usually taken into account by a scaling factor (last column in Table I).

B. Defects after electron irradiation

An increase in the average lifetime of about 30 ps indicates the presence of a high density of open-volume defects in the as-irradiated state (2 MeV electron energy, dose of $10^{18}$ cm$^{-2}$). A decomposition of the spectra is not possible in the annealing range between 90 and 250 K and at the measurement temperature of 90 K. This is in accordance with the observations in electron-irradiated III–V compounds, and it is due to the competitive trapping of positrons in shallow positron traps as well as in vacancylike defects (see the discussion below). The average positron lifetime of about 260 ps indicates the presence of open-volume defects larger than monovacancies, i.e., most probably divacancies. Although no decomposition of the spectra is possible, this conclusion can be drawn, since the average lifetime exceeds the calculated value of monovacancies, which is 257 ps at maximum (see Table I).

Figure 4 shows the annealing behavior of irradiated $CuInSe_2$, reflected in a sharp decrease in the average positron lifetime in the range between the temperature of sample installation (90 K) and 250 K.

As explained above, we conclude that divacancies detectable by positrons disappear in the main annealing stage. It is not possible to distinguish between several kinds of divacancies because there is no information so far about ionization levels, charge states, and dominating kind of divacancies.

The determination of defect introduction rates of the electron irradiation is rather complicated due to the lacking spectra decomposition at low temperatures. The reason is the
competitive trapping between shallow traps and open-volume defects and its complex temperature dependence. Thus, the attempt of determining the vacancy-defect introduction rate yields only a lower-limit estimation. We used the average lifetime obtained at 90 K after irradiation and transfer of the sample to the cryoheater system, \( \tau = 266 \text{ ps} \). The defect-related lifetime for divacancies is used in order to determine the positron trapping rate \( \kappa \) (see the discussion above). This value is taken as the average over the three theoretically calculated divacancy lifetimes, \( \tau_2 = 293 \text{ ps} \). \( \kappa \) was obtained according to Eq. (1), \( \kappa = 4.7 \times 10^9 \text{ s}^{-1} \). The influence of shallow traps on this calculation of \( \kappa \) is ignored, leading to a too low trapping rate of divacancies. Therefore, only a lower-limit estimation for their concentration is obtained. Using a trapping coefficient of 0.03 and 0.3 cm\(^{-1}\) was reported for low-temperature electron irradiation of \( p^- \) and \( n^+ \)-type Si, respectively.\(^{32}\) An introduction rate of about 1 cm\(^{-3}\) was given for electron-irradiated GaAs (\( T_{\text{irr}} = 4 \text{ K} \)).\(^{33}\) The total introduction rate can, nevertheless, reach a very high value; \( \approx 7 \text{ cm}^{-1} \) was found for GaAs in one sublattice.\(^{33}\) The defect concentration of shallow traps (see the discussion below) suggests also a higher total introduction rate for CIS.

This lower-limit estimation of the introduction rate is comparable to other elemental and compound semiconductors. A value of 0.03 and 0.3 cm\(^{-1}\) was reported for low-temperature electron irradiation of \( p^- \) and \( n^+ \)-type Si, respectively.\(^{32}\) An introduction rate of about 1 cm\(^{-3}\) was given for electron-irradiated GaAs (\( T_{\text{irr}} = 4 \text{ K} \)).\(^{33}\) The total introduction rate can, nevertheless, reach a very high value; \( \approx 7 \text{ cm}^{-1} \) was found for GaAs in one sublattice.\(^{33}\) The defect concentration of shallow traps (see the discussion below) suggests also a higher total introduction rate for CIS.

The positron lifetime reaches 235 ps, i.e., the positron bulk lifetime after annealing at about 250 K and at a measurement temperature of 90 K. This experimental result can be explained either by the decrease in the concentration of open-volume defects below the sensitivity limit of positron annihilation, or by the fact that possibly existing vacancy-type defects are positively charged. A further possibility would be the existence of shallow positron traps, which are completely dominating the positron trapping. The latter case can be excluded by temperature-dependent positron lifetime measurements, since the shallow traps should lose their trapping efficiency at high temperatures (see Sec. III). The result of corresponding experiments performed after annealing at 265 and 340 K is shown in Fig. 5. Only a slight increase in the average positron lifetime was observed, indicating that only the first two explanations given above have to be taken into account. Hence, we conclude that no neutral or negatively charged open-volume defects are present in a considerable amount in the annealing temperature range between 250 and 400 K.

A further increase in the average lifetime is detectable above 450 K (see Fig. 4). Obviously, a new defect type is formed in this annealing range. A possible cause could be the evaporation of one of the components of the ternary com-

![FIG. 5. The lower panel shows the average positron lifetime as a function of measurement temperature in electron-irradiated (\( E = 2 \text{ MeV}, \Phi = 10^{19} \text{ cm}^{-2}, T = 4 \text{ K} \)) CuInSe\(_2\) after different annealing steps. The fitted curve (solid line) corresponds to the two-defect trapping model and is drawn for the state after the 580 K annealing step. The upper panel shows the defect-related lifetime obtained as a result of the two-component spectra decomposition after annealing at 580 K. The spectra decomposition could only be performed at higher temperatures due to competitive trapping by shallow traps in the low-temperature range.](image-url)
detected. It is known that Cu and In atoms become mobile at an annealing temperature of about 570 K ($D_{\text{Cu}} = 1.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{In}} = 1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$). The diffusion coefficient of Se atoms is comparably very small ($D_{\text{Se}} < 1 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) at this temperature.

We assume that this defect type is created during annealing above 450 K due to a defect reaction of irradiation-induced defects invisible for positions. Obviously, the primary annealing stage up to 250 K does not lead to a complete annealing of the radiation defects. Part of the defects survives the annealing stage that is completed below 250 K as defects invisible for positrons. Possible candidates are defects or defect complexes containing no vacancies. In the case that vacancies are part of the complex, it must be concluded that the complex, or at least the vacancy, is positively charged. Therefore, one has to conclude that at least three different defect types are involved in the annealing behavior up to 600 K.

In order to confirm that this “invisible” defect is caused by the irradiation, an annealing experiment was performed with an unirradiated reference sample. No change of the average positron lifetime was observed during an annealing up to 1000 K.

Using the trapping model, we attempted to fit the positron lifetime taking into account a negatively charged open-volume defect. The fitting curve is identical with that of the other model (neutral divacancy), and the obtained quantities are also physically reasonable. Therefore, we cannot distinguish between neutral or negatively charged divacancies by our temperature-dependent experiments. Positively charged defects are expected to repel positrons and they should, thus, be no positron traps.

VII. CONCLUSIONS

CulnSe$_2$ was studied after low-temperature (4 K) 2 MeV electron irradiation. No positron trapping was observed for the unirradiated sample, indicating that the concentration of neutral and negatively charged vacancies is smaller than 5 \times 10^{15} \text{ cm}^{-3}. The positron bulk lifetime was determined to be 235 ps.

An increased average positron lifetime indicates the appearance of divacancy-type defects after the first annealing step during assembling the irradiated sample into the cryostat. A lower-limit estimation of their introduction rate yields a value of 0.02 cm$^{-1}$. The average positron lifetime reaches the bulk value during the annealing treatment up to 250 K and increases again at annealing temperatures above 450 K. It is concluded that defect complexes undetectable by positrons exist in the temperature range between 250 and 450 K. These are mostly complexes without vacancies or positively charged defect complexes containing vacancies. They undergo above 450 K a further defect reaction leading to a divacancy signal of thermally more stable complexes. Obviously, new neutral or negatively charged divacancy defects are created with a concentration of about 1 \times 10^{15} \text{ cm}^{-3}.

A large number of shallow positron traps was detected after electron irradiation. Thus, further irradiation-induced defects exist in addition to the observed vacancy defects, which are negatively charged and exhibit no open volume. The CulnSe$_2$ antise site defect is the dominating acceptor in the investigated material according to a simple defect-chemical approach, and may be responsible for the positron trapping in these shallow positron traps.
ACKNOWLEDGMENTS

Dr. F. Dworschak from Forschungszentrum Jülich is kindly acknowledged for carrying out the electron irradiations. The authors thank Professor D. Cahen (Weizmann Institute of Science, Israel) for his valuable discussion. The studies are supported by the German–Israel Foundation for Scientific Research and Development, the Deutsche Forschungsgemeinschaft, and the Vereinigung der Freunde und Förderer der Martin-Luther-Universität Halle-Wittenberg e.V.