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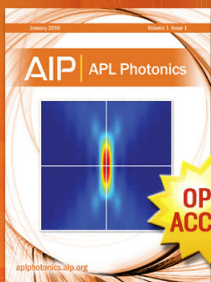Positron annihilation in (Ga, Mn)N: A study of vacancy-type defects
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Native vacancy defects in $Zn_{1-x}(Mn,Co)_xGeAs_2$ studied with positron annihilation spectroscopy

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We have studied vacancy defects in chalcopyrite semimagnetic semiconducting mixed $Zn_{1-x}(Mn,Co)_xGeAs_2$ bulk crystals with alloy composition x varying between 0.052 to 0.182 using positron annihilation spectroscopy. We identified As vacancies, potentially complexed with the transition metal alloying elements, in all the studied samples, while no cation vacancy related defects were detected. The positron lifetimes for the bulk $ZnGeAs_2$ lattice and neutral As vacancy were determined to be $\tau_B = 220-230$ ps and $\tau_{As} = 300 \pm 10$ ps, respectively. Our results also show that the p-type conductivity in the samples is not due to cation vacancy related acceptor centers. The As vacancies were found to be present at such low concentrations that they cannot be responsible for the compensation of the p-type conductivity or the reduction of mobility in the $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3168440]

I. INTRODUCTION

The limited possibilities of miniaturization of electronic complementary metal oxide semiconductor (CMOS) devices have led researchers to explore new ways of processing information. One of the widely tested ideas that may revolutionize modern electronics is the idea of using both the charge and the electron spin to transmit information. The newly created class of spintronic[1] devices that possess the capabilities to produce and detect spin polarized carriers is one of the potential candidates that may revolutionize modern electronics. For the construction of spin electronic devices, it is necessary to develop materials, which combine semiconducting (with the ability to change the electrical properties through doping or other methods) and magnetic (showing ferromagnetic ordering at room temperature) properties.

Diluted magnetic semiconductors (DMS) offer very promising physical properties, which put them in the forefront of candidates for applications in spin electronics. Most materials are created using semiconductor matrix based on III–V or II–VI compounds, to which paramagnetic ions such as transition metal (TM) ions (Mn, Co, Fe) or rare earths (Gd, Eu, Sm) are added.[2–4] The inclusion of magnetic ions into the semiconductor allows the creation of a material in which you can control the magnetic properties by changing the electrical properties of the alloy. This is possible because the ferromagnetism in DMSs is mediated by the conducting carriers. This is extremely useful in the context of engineering materials and potential applications. The most intensively

investigated DMS is $Ga_{1-x}Mn_xAs$, in which it is possible to tune Curie temperature, T_C, in a wide range of temperatures (up to 173 K).[5]

Most literature reports on the magnetic properties of DMS give a Curie temperature much lower than room temperature, which makes such materials impractical for possible applications. The lack of appropriate semimagnetic semiconductors among materials based on III–V and II–VI compounds, i.e., capable of working at room temperature, has forced the search for new ferromagnetic semiconductors that meet these requirements. Among many of the newly discovered ferromagnetic semiconductors exists a very promising group of materials in which the ferromagnetism was discovered at temperatures higher than 300 K. This class consists of several II–IV-V_2 chalcopyrite compounds such as $Cd_{1-x}Mn_xGeP_2$ (Ref. 6) or $Zn_{1-x}Mn_xSnAs_2$ [7,8] with T_C equal to 320 and 329 K, respectively.

In the present article we investigate the $Zn_{1-x}(Mn,Co)_xGeAs_2$ compound, whose chemical composition varied between $0.052 \leq x \leq 0.182$. The nonmagnetic equivalent of this alloy has many interesting physical properties. For example, the top of the valence band is nondegenerate, which means that this material is an effective source of spin polarized photoelectrons.[9] In addition, the large nonlinear optical coefficients are such that $ZnGeAs_2$ is suitable for applications in nonlinear optics.[10] This material has a direct energy gap at the Γ point of the Brillouin zone with a value of $E_g = 1.15$ eV, which expands its potential applications for optoelectronic devices.[11] Moreover, this material has a lattice constant similar to GaAs,[12] which makes it compatible with existing technology. In our previous work[13] we have shown the existence of ferromagnetic ordering of the $Zn_{1-x}Mn_xGeAs_2$ alloy (with $x \geq 0.078$) with Curie temperature far above room temperature ($T_C = 367$ K for $x = 0.182$). We believe that the observed room temperature ferromag-

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TABLE I. Results of basic characterization of Zn$_{1-x}$(Mn,Co)$_x$GeAs$_2$ samples including: molar fractions of substitutional TM ions x, crystallographic parameters a and c, and transport properties measured at room temperature including free carrier concentration n, resistivity ρ_{xx}, and mobility μ.

TM	x	a (Å)	c (Å)	n (10^{19}) (cm^{-3})	ρ_{xx} (10^{-2}) (Ω cm)	μ (cm^2 V^{-1} s^{-1})
Co	0.052	5.673	11.149	3.8 ± 0.2	2.1 ± 0.1	10 ± 0.5
Mn	0.053	5.658	11.242	3.5 ± 0.2	1.6 ± 0.1	11 ± 0.5
Mn	0.078	5.651	11.232	5.2 ± 0.3	4.6 ± 0.2	2.6 ± 0.2
Mn	0.182	5.654	11.197	7.5 ± 0.4	3.4 ± 0.2	2.4 ± 0.2

netism was related to the spinodal distribution of magnetic ions in the semiconductor.[14] It should also be noted that the electrical properties of the alloy depend strongly on its chemical composition. The samples had p-type conductivity with carrier concentration n between 10^{19}–10^{20} cm^{-3} and mobility $\mu \approx 10$ cm^2 V^{-1} s^{-1}.

In order to explain the observed electrical and magnetic properties of this alloy we have studied vacancy-type defects using positron annihilation spectroscopy. Positrons implanted into a solid can get trapped in, and localize at, neutral and negative vacancies due to the missing positive ion core. This results in observable changes in the measurable annihilation characteristics, i.e., the positron lifetime, and the momentum distribution of the annihilating positron-electron pair, which can be detected using Doppler broadening spectroscopy. The annihilation parameters can be used to determine the vacancy concentration as well as to distinguish between different vacancy types and their chemical environment. Typically, native vacancy defects are important for electrical compensation of semiconductor materials. They may also affect magnetic properties of DMS. Due to these facts, the present studies are crucial to understand and control the properties of Zn$_{1-x}$(Mn,Co)$_x$GeAs$_2$ crystals. The present investigations may also be of help in making future improvements in the growth technology of these alloys.

II. EXPERIMENTAL

A. Sample preparation and basic characterization

For purposes of our investigations we have prepared bulk Zn$_{1-x}$(Mn,Co)$_x$GeAs$_2$ mixed crystals grown by the direct fusion method from a stoichiometric ratio of high purity powders of ZnAs$_2$, Mn, and Ge. The details about the growth procedure can be found in Ref. 15. In order to increase the Mn solubility in the alloy, the crystals were cooled down from the growth temperature ($T \approx 1170$ K) with high speed of 5–10 K/s. The crystals were then cut into thin slices (about 1 mm thick) perpendicular to the growth direction.

For the basic electrical characterization of the samples, we used standard six contact Hall configuration. Electrical contacts to the sample were prepared on an etched and polished surface using indium solder and gold wires. We measured the resistivity ρ_{xx} parallel to the current direction. The Hall effect measurements were performed in the constant magnetic field $B = 1.4$ T.

B. Positron annihilation spectroscopy

The positron lifetimes in 0.5 mm thick samples were measured with a conventional fast-fast coincidence spectrometer with a time resolution of 250 ps.[16] Two identical sample pieces were sandwiched with a 20 μCi ^{22}Na positron source. Typically 4×10^6 annihilation events were collected in each positron lifetime spectrum. The lifetime spectrum, $n(t) = \Sigma_i \tau_i I_i \exp(-t/\tau_i)$, was analyzed as the sum of exponential decay components convoluted with the Gaussian resolution function of the spectrometer, after subtracting the constant background and annihilations in the source material (typically a few percent, for details see, e.g., Ref. 17). The positron in state i annihilates with a lifetime τ_i and an intensity I_i. The state in question can be the delocalized state in the lattice or the localized state at a vacancy defect. The increase in the average lifetime $\tau_{av} = \Sigma_i I_i \tau_i$ above the bulk lattice lifetime, τ_B, shows that vacancy defects are present in the material. This parameter is insensitive to the decomposition procedure, and even a change in its value as small as 1 ps can be reliably measured.

In the case of one type of vacancy defect with specific lifetime τ_V, the decomposition of the lifetime spectrum into two components τ_1 and τ_2 is straightforward to interpret. The second lifetime component, $\tau_2 = \tau_V$, gives directly the vacancy specific lifetime and the first lifetime component is $\tau_1 = (\tau_B^{-1} - \kappa_V)^{-1}$, where τ_B is the positron lifetime in the delocalized state in the lattice and κ_V is the positron trapping rate into the vacancy defects.

The Doppler broadening of the annihilation radiation was measured simultaneously with the positron lifetime. In this setup a Ge detector with an energy resolution of 1.3 keV was used. The conventional S (low momenta: $|p_z| < 0.4$ a.u.) and W (high momenta: 1.5 a.u. $< |p_z| < 4.0$ a.u.) annihilation parameters were determined from the measured data after background subtraction as the fractions of annihilations in the corresponding momentum ranges.

III. RESULTS AND ANALYSIS

The chemical composition of crystals was checked using x-ray fluorescence spectroscopy. The results showed that the chemical composition of crystals along the ingot was uniform indicating that the bulk crystals are homogeneous. The chemical compositions of the samples are gathered in Table I. Typical relative uncertainty of this method is about 10%.

In order to have information about the crystallographic quality of our samples we performed standard powder x-ray
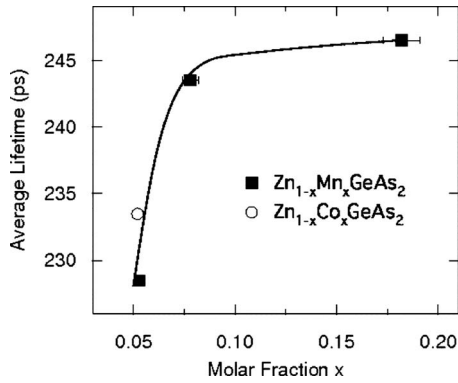
FIG. 1. Average positron lifetime τ_{av} as a function of TM ion molar fraction x measured for $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples containing Mn (closed points) and Co (open points) ions. The line is a guide to the eye and indicates the trend in τ_{av} with x.

diffraction (XRD) spectroscopy measurements on each sample. The results showed that the grown samples were single phase and crystallized in the chalcopyrite structure. For Mn content $x < 0.08$ the samples were single crystals, while for $x > 0.08$ the samples were polycrystalline with grain size in the 5 nm range. One additional sample with Co instead of Mn was also a single crystal. The lattice parameters obtained from XRD measurements are also gathered in Table I. Comparison of unit cell volume of our alloy compositions with results from literature for $ZnGeAs_2$ and $MnGeAs_2$ shows that the samples exhibit bowing nonlinearity different from the Vegard law: the unit cell volume exhibits a minimum at $x \approx 0.182$.

In addition to the standard crystallographic characterization we also performed a basic electrical characterization of the samples, including measurements of electrical resistivity and Hall carrier concentration at room temperature. These results are also gathered in Table I.

The average positron lifetime measured in the $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples is shown in Fig. 1. It is clearly seen that the average lifetime increases with increasing TM content, indicating that (i) vacancy defects are observed in the samples and (ii) the total open volume contained in the observed vacancy defects increases when the TM content is increased. Further, alloying with Co instead of Mn (at similar content) with $ZnGeAs_2$ results in a higher amount of open volume defects. The data presented in Fig. 1 were measured at room temperature. Measurements as a function of temperature in the range 10–400 K were also performed, but no changes in the average positron lifetime could be observed at these temperatures.

The positron lifetime spectra measured in the four samples could be decomposed into two components, τ_1 and τ_2, giving the value $\tau_2 = 290-310$ ps for the higher component. The results of the decomposition of the lifetime spectra are given in Table II, together with the estimation of the bulk lifetime assuming that only one kind of defect contributes to the positron lifetime: $\tau_B = \tau_1\tau_2/(\tau_1 + \tau_2 - \tau_{av})$.[16] The estimated bulk lifetime of about 220–230 ps is similar to that in the binary counterpart of $ZnGeAs_2$, namely, GaAs (with similar lattice constant), where $\tau_B = 230$ ps.[18] This suggests that the one-defect model is applicable in this case and that the estimated bulk lifetime can be assumed to be the actual positron lifetime in the defect-free lattice of $ZnGeAs_2$. The behavior of the first (lower) lifetime component also supports the use of the one-defect model, as it decreases with increasing average positron lifetime and increasing positron trapping at vacancies. The higher lifetime component is the lifetime of positrons trapped at vacancy defects.

In order to study the possible chemical effects of transition metals on the observed vacancies in the $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples we measured the Doppler broadening of the annihilation line simultaneously with the positron lifetime. The S and W parameters determined from the spectra are shown in Table II together with the lifetime data. The Doppler broadening parameters (S and W) behave in a manner similar to the average lifetime, i.e., the S parameter increases and the W parameter decreases with increasing TM content, as is typical when the amount of open volume increases.

Plotting the measured S and W parameters in an (S,W) plane shows that they all form a line (Fig. 2). This indicates again that there are two kinds of states where the positrons annihilate. One is the defect state characterized by the higher lifetime component of $\tau_2 = 300 \pm 10$ ps, and the other state is the free state of the positron in the perfect lattice. However, the sample alloyed with Co does not follow the general single-defect trend of increasing S (decreasing W) parameter with increasing open volume. This effect is best observed when the S and W parameters are plotted as a function of the average positron lifetime (Fig. 3). If there were only one kind of defect in all samples, the S and W parameters and τ_{av} would all depend on each other linearly.[16] However, as can be very clearly seen in Fig. 3, both the S and W parameters measured in the sample alloyed with Co fall out of the line that can be drawn through the rest of the data.

It is likely that the S and especially the W parameters in the sample alloyed with Co reflect a change in the chemical environment (change in electron configuration) of the ob-

TABLE II. The average positron lifetime, τ_{av}, the two lifetime components, τ_1, τ_2, and the intensity I_2 ($I_1 = 1 - I_2$) extracted from the experimental lifetime spectra, the chi-square value for the decomposition χ^2, and the bulk lifetime τ_B in $Zn_{1-x}(Mn,Co)_xGeAs_2$ estimated applying the one-defect model, and Doppler broadening spectra characteristic S and W parameters.

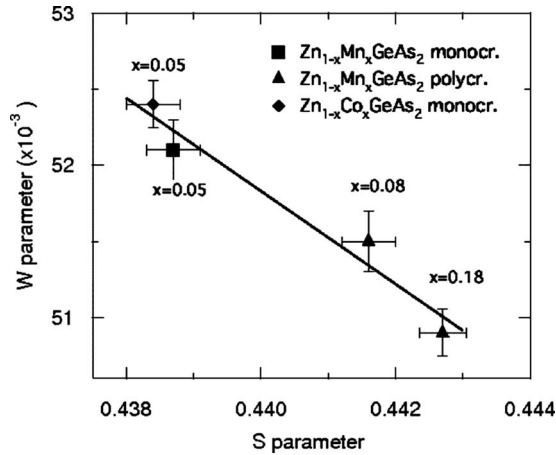| TM	x	τ_{av} (ps)	τ_1 (ps)	τ_2 (ps)	I_2 (%)	χ^2	τ_B (ps)	S	W
Co	0.052	233.5 ± 0.5	195 ± 3	302 ± 4	36 ± 3	1.16	223 ± 5	0.4384	0.0524
Mn	0.053	228.5 ± 0.5	197 ± 3	288 ± 5	35 ± 4	1.02	220 ± 5	0.4387	0.0521
Mn	0.078	243.5 ± 0.5	183 ± 3	297 ± 2	53 ± 2	1.02	229 ± 5	0.4416	0.0515
Mn	0.182	246.5 ± 0.5	188 ± 3	310 ± 3	49 ± 2	1.14	231 ± 5	0.4427	0.0509

FIG. 2. W vs S parameter obtained for $Zn_{1-x}(Mn,Co)_xGeAs_2$ mixed crystals with different TM ion content x (shown in labels).

served vacancies. Both the alloying elements, Mn and Co, substitute for Zn in $ZnGeAs_2$. As positrons trapped at vacancies are sensitive to changes only in the neighboring atoms, this suggests that the vacancy defects observed by positrons are located on the As sublattice, with nearest neighbors from the Zn and Ge sublattices.

IV. DISCUSSION

The results of the positron experiments can be better understood by comparing them to those obtained in the binary counterpart of $ZnGeAs_2$, namely, GaAs. The chalcopyrite structure of $ZnGeAs_2$ is nearly the same as the zincblende structure of GaAs with the Ga atoms substituted by atoms neighboring Ga ($Z=31$), half by Zn ($Z=30$), and the other half by Ge ($Z=32$). As the lattice constants of these two materials are very similar, it is natural to assume that the positron lifetime parameters of the defect-free crystal lattices are similar. The Doppler parameters are much more sensitive to the details of both the atomic and electronic structures that affect the penetration of the positron wave function to the electron shells around the ions and should not be expected to be similar. The latter is illustrated very well by comparing
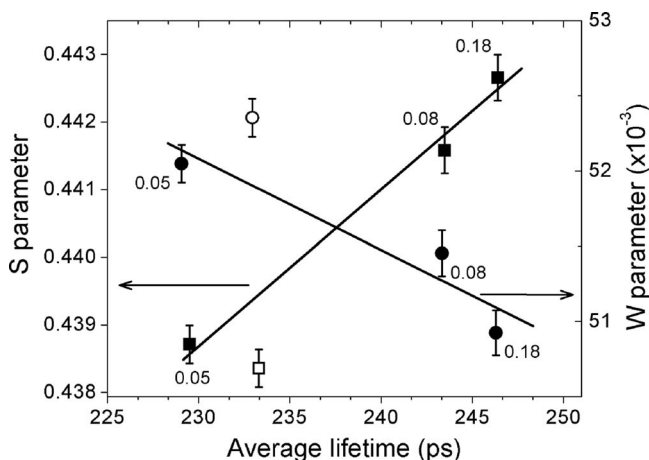

FIG. 3. The W (circles) and S (squares) parameters plotted as a function of the average positron lifetime τ_{av} for Mn (closed symbols) and Co (open symbols) alloyed $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples.

ZnO and GaN: they both crystallize in the hexagonal wurtzite structure, the atoms forming the compounds are nearest neighbors in the periodic table of elements, and the lattice constants are similar (a bit larger in ZnO). The positron lifetime in the bulk lattice is (about 5%) higher in ZnO than GaN, the S parameter is 5% lower and the W parameter 30% higher. Notice for comparison that a 5% increase in lifetime in one material due to vacancies is typically accompanied by a change in the Doppler parameters of much lower magnitude than the difference between materials.[19,20]

Indeed, the bulk lifetime estimated from the present data on $ZnGeAs_2$, $\tau_B=220-230$ ps, is very close to the value obtained in GaAs: $\tau_B=230$ ps.[18] The values for τ_B in Table II are all within experimental accuracy. It is worth noting, however, that the bulk lifetime must be equal to or smaller than the measured average positron lifetime. Hence the bulk lifetime must be below the average lifetime measured in the sample with 5% of Mn ($\tau_{av}=228$ ps). In addition, as this sample already contains vacancy defects, 220 ps can be taken as the bulk lifetime. The higher bulk lifetimes estimated from the polycrystalline samples can be affected by the presence of some other open volume defect and trapping at the grain boundaries.

The second (higher) lifetime component that can be separated from the lifetime spectra is roughly the same in all the four samples, namely $\tau_2=290-310$ ps. In the case of GaAs, the Ga sublattice vacancy has a lifetime of about 260 ps, and the As vacancy about 295 ps in the neutral and about 260 ps in the negative charge state.[18] Hence, as the bulk lifetime is quite similar in both $ZnGeAs_2$ and GaAs, it is natural to assign the second lifetime component measured here to As vacancies. The sensitivity of the Doppler parameters to the alloying element suggests that the As vacancies are formed preferentially next to Mn or Co, both substituting for Zn. The difference in the annihilation of positrons for the two elements comes from the fact that the Co atoms have more $3d$ electrons than the Mn atoms. The contribution from the additional $3d$ electrons to the high momentum part of electron density should increase the W parameter.[21] This reasoning is supported by our calculations of the core electron momentum distributions in $ZnGeAs_2$ and representative vacancy defects, where we solved the positron state and constructed the electron density of the wave function of the free atoms, similar to the manner described in Ref. 22. The results of the calculations show that Co decoration of the As vacancy indeed produces a higher W parameter than Mn decoration.

At this point it is worth considering that the lack of temperature dependence in the positron data could in principle be due to the metallic screening by the acceptor centers, which are responsible for the high p-type conductivity. This effect of metallic screening has been observed in the binary counterpart of $(Zn,Mn)GeAs_2$, p-type $(Ga,Mn)As$, where the hole concentration was 10^{20} cm^{-3} or greater.[23] In the present samples the hole concentration is in the mid-10^{19} cm^{-3} range, and hence we find that the lack of temperature dependence in the positron data indicates that the observed vacancies are in the neutral charge state, giving further support to our interpretation of the higher lifetime component being due

to As vacancies. As the samples are quite highly *p*-type and the formation enthalpy of negatively charged defects is high due to the Fermi energy being close to the valence band maximum and cation vacancies in compound semiconductors have a tendency to be acceptorlike (negatively charged), we note that it is rather natural to find neutrally charged donorlike As vacancies in ZnGeAs$_2$. It is interesting that no traces of As vacancies were found in the above-mentioned (Ga,Mn)As in a wide range of Mn content, but only Ga vacancies, which should not be easily formed in *p*-type material, were observed. The explanation for this apparent discrepancy is probably in the growth method of the (Ga,Mn)As samples: they were grown by As-rich low temperature molecular beam epitaxy (LT-MBE), where the formation of As vacancies is suppressed and that of Ga vacancies enhanced. In fact, instead of As vacancies, As antisite defects are abundant in LT-MBE GaAs.

We want to emphasize here that no other open volume defects than As vacancies were observed in the Zn$_{1-x}$(Mn,Co)$_x$GeAs$_2$ samples studied in this work. If cation vacancies were present, they probably would be in the negative charge state and would be much more attractive trapping centers for positrons than the neutral As vacancy complexes, especially at low temperatures. However, no trace of negative defects, or vacancy defects of cation vacancy size, could be observed. In addition, the trapping of positrons to the observed As vacancies is not in saturation, an effect that could prevent (if present) the observation of other defects. Hence the *p*-type conductivity of the material cannot be explained by the Zn or Ge vacancies, which have been proposed to act as shallow acceptor dopants.[24]

The concentrations of the As vacancies in the samples can be estimated from the experimental data, assuming a positron trapping coefficient, μ_V, around 1×10^{15} s^{-1}, the value typical of neutral vacancies,[18] as $[V_{As}] = N_{at} \times \mu_V^{-1} \tau_B^{-1}(\tau_{av} - \tau_B)/(\tau_D - \tau_{av})$, where $\tau_D = \tau_2$ and $N_{at} = 4.2 \times 10^{22}$ cm^{-3} is the atomic density of ZnGeAs$_2$. This results in $[V_{As}]$ value around 2×10^{16} cm^{-3} in the samples with 5% of TM alloying element and $[V_{As}] = 2 \times 10^{17}$ cm^{-3} in the polycrystalline samples with 8% and 18% of Mn. It is worth noting that the vacancy concentrations are very likely to be the same in the samples with 5% of Mn and Co. The 5 ps difference in the average lifetime originates from the 15 ps difference in the second lifetime components, the intensities of which are about 35% in both samples (see Table II). There is no appreciable difference in the defect concentrations between the two polycrystalline samples, where the intensities of the second lifetime components are both about 50%. Hence, it seems that the concentration of the neutral As vacancies is determined by the crystalline quality rather than by the TM content. It suggests that the As vacancies could be preferentially formed at grain boundaries, as their concentrations are clearly higher in the polycrystalline than in the monocrystalline samples.

The comparison of the concentrations of the neutral As vacancy complexes to the carrier (hole) concentrations in Table I shows that these complexes are not efficient compensating centers because their concentrations are more than two orders of magnitude lower than those of the carriers in the single crystals and in the polycrystalline samples. In addition, as they are neutral, the As vacancy complexes are not likely to act as efficient scattering centers for carriers and are not responsible for the reduction of the mobility in the polycrystalline samples. The decrease in the mobility in the polycrystalline samples is probably related to the carrier scattering at grain boundaries. It should be noted, though, that the detection of positively charged defects—including positively charged As vacancies that are likely to exist in *p*-type material—is not possible using positrons. Hence the possibility of these defects affecting significantly the carrier concentration and mobility cannot be excluded.

V. SUMMARY

We have performed studies of vacancy type defects in Zn$_{1-x}$(Mn,Co)$_x$GeAs$_2$ mixed crystals grown by the direct fusion method. Basic characterization showed that we have obtained both mono- and polycrystalline *p*-type conductive samples with substitutional ion composition, *x*, ranging from 0.052 up to 0.182. By comparison to well-known results in GaAs we interpret results obtained with the positron annihilation spectroscopy as neutral As vacancies being present in all the studied samples. The results further suggest that the As vacancies are complexed with the TM alloying elements. No traces of other vacancy defects, especially in the cation-sublattice, could be found. We determined experimentally the positron lifetime in the ZnGeAs$_2$ lattice to be $\tau_B = 220 - 230$ ps and $\tau_{As} = 300 \pm 10$ ps in the neutral As vacancy. Our results also show that the *p*-type conductivity in the samples is not due to cation vacancies, and must be related to other characteristics—possibly another kind of nonstoichiometry—of the crystal lattice. The neutral As vacancy complexes were found to be present at relatively low concentrations and they cannot be responsible for the compensation of the *p*-type conductivity or the reduction of mobility in the Zn$_{1-x}$(Mn,Co)$_x$GeAs$_2$ samples.

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