Identification of the Native Vacancy Defects in Both Sublattices of ZnS_xSe_{1-x} by Positron Annihilation

K. Saarinen, T. Laine, K. Skog, J. Mäkinen, and P. Hautojärvi
Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

K. Rakennus, P. Uusimaa, A. Salokatve, and M. Pessa
Department of Physics, Tampere University of Technology, P.O. Box 692, 33101 Tampere, Finland

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We show how positron annihilation can distinguish vacancies in the different sublattices of a binary compound by performing experiments in ZnS_xSe_{1-x} layers. We identify the Se vacancies (V_{Se}) in N-doped and the Zn vacancies (V_{Zn}) in Cl-doped material by the shape of the core electron momentum distribution. The charge of the defect involving V_{Se} is neutral or negative in p-type ZnS_xSe_{1-x}, suggesting that V_{Se} is complexed with an acceptor. The concentration of the V_{Se} complexes is high ($\geq 10^{18}$ cm^{-3}), indicating that their role is important in the electrical compensation of p-type ZnS_xSe_{1-x}. [S0031-9007(96)01393-2]

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ZnSe has attracted strong interest as a potential material for blue-green diode lasers, since its band gap is wide (2.67 eV) and its lattice constant matches closely to that of GaAs substrates. However, fundamental problems exist in the doping: ZnSe can be easily doped n type but the fabrication of p-type material is still difficult. With nitrogen doping the active acceptor concentration saturates at about 10^{18} cm^{-3}, although more than 10^{19} cm^{-3} N atoms have been incorporated during the growth. In fact, similar doping problems have been detected in many wide-band-gap sulfides and selenides, which suggests that these phenomena may have a common microscopic nature.

Several theoretical models have been proposed for the origin of the doping problems. The simplest explanation is that native defects compensate the doping atoms. Theoretical calculations have suggested, however, that the concentration of spontaneously formed point defects is too low to cause substantial compensation [1]. On the other hand, the recent calculations of Garcia and Northrup [2] show that a high concentration of defect complexes involving the N dopant and donor defects can be formed in the lattice. Another kind of explanation for the doping problems is the existence of a limit for the solubility of impurities [3]. It has also been proposed that large atomic displacements near the dopant atoms can play an important role in passivation [4,5]. These models include the formation of defects analogical to the *DX* center in AlGaAs [6] and the recently proposed lattice instability leading to two broken bonds in the proximity of the acceptor atom [7]. However, very little experimental data exist on the microscopic origin of the compensation in ZnSe.

In this work we apply positron annihilation spectroscopy to study the vacancy defects in ZnS_xSe_{1-x} and their role in the compensation. We show how the sublattices of the vacancies can be directly identified in the experiments by the shape of the core electron momentum distribution. We detect Se vacancies in N-doped and Zn vacancies in Cl-doped ZnS_xSe_{1-x}. The charge state of the Se vacancy is neutral or negative in p-type ZnS_xSe_{1-x}, suggesting that it is complexed with an acceptor, possibly with the nitrogen dopant. The vacancy concentration in heavily N-doped ZnS_xSe_{1-x} is at least 10^{18} cm^{-3}, which indicates that the Se vacancy can play an important role in the electrical compensation of p-type ZnS_xSe_{1-x}.

The samples in this work were 2 μm $ZnS_{0.06}Se_{0.94}$ overlayers grown by molecular beam epitaxy (MBE) as lattice matched on a GaAs substrate. The alloy composition $x = 0.06$ varied less than 1% from one sample to another according to the x-ray diffraction experiments. A $ZnCl_2$ effusion cell was used for Cl doping and a N_2 plasma source for the N doping. The impurity concentrations were determined by secondary ion mass spectrometry (SIMS). The N concentrations varied in the range of $[N] = (1-30) \times 10^{18}$ cm^{-3} in the six studied samples, depending on the power of the N_2 plasma source. The electrochemical capacitance-voltage profiling (ECV) showed that the hole concentration is at maximum 2×10^{17} cm^{-3}, thus indicating that most of the nitrogen acceptors are electrically inactive. In the two Cl-doped samples both the n-type carrier and the Cl concentrations were roughly 10^{18} cm^{-3} according to ECV and SIMS experiments.

The positron experiments were performed using a positron beam at the energy of 15 keV corresponding to a mean positron stopping depth of 0.5 μm. This energy was chosen so that all positrons annihilate in the ZnS_xSe_{1-x} overlayer. The Doppler broadened shape of the 511 keV annihilation radiation was measured with a Ge detector and described with the conventional valence and core annihilation parameters S and W [8]. The S parameter represents the fraction of positrons annihilating mainly with the valence electrons with a longitudinal momentum component of $p_L \leq 3.7 \times 10^{-3}\ m_0c$, where m_0 is the electron mass and c the speed of light. The

W parameter is the fraction of annihilations with the core electrons with a large momentum component of $11 \times 10^{-3}\, m_0 c \leq p_L \leq 29 \times 10^{-3}\, m_0 c$. The detailed shape of the core electron momentum distribution was studied by the coincidence measurement of Doppler broadening, in which the two annihilation quanta are detected simultaneously [9]. This technique enables the observation of longitudinal electron momenta up to $p_L \approx 40 \times 10^{-3}\, m_0 c$.

Positrons get trapped at neutral and negative vacancy defects because of the missing positive charge of the ion cores. The reduced valence and core electron density at a vacancy increases the positron lifetime and narrows the positron-electron momentum distribution. Consequently, the valence annihilation parameter S increases and the core annihilation parameter W decreases. The momentum distribution of the annihilated core electrons contains information on the atomic numbers of the ions. A trapped positron at a vacancy overlaps mainly with the core electrons of the nearest neighbor atoms. Hence the shape and magnitude of the core electron momentum distribution can be used to identify the sublattice of the vacancy acting as a positron trap [9].

Figure 1 shows the temperature dependence of the valence annihilation parameter S in some of the studied samples. In N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ the S parameter increases with temperature more strongly than in undoped and Cl-doped material, while its absolute value is smaller. A similar but reverse effect is observed in the W parameter, which is clearly larger in N-doped than in undoped and Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. At low temperature of 20–100 K the S parameter anticorrelates with the nitrogen concentration: when [N] increases, the S parameter is lower.

The S parameter in the $[\mathrm{N}] = 4.8 \times 10^{18}\ \mathrm{cm}^{-3}$ doped sample increases by more than 2% with temperature at 20–300 K. This increase is much larger than that of roughly 0.1% per 100 K we have measured for delocalized positrons in defect-free Si, GaAs, and InP. The temperature dependence can thus only be explained by positron trapping at vacancy defects: The S parameter behaves as in Fig. 1, when the fraction of positron annihilations at vacancies increases with temperature. This can be due to shallow positron traps or, in p-type samples, also due to the ionization of the vacancy [8,10]. In the other layers the S-parameter values are even larger than those obtained in the $[\mathrm{N}] = 4.8 \times 10^{18}\ \mathrm{cm}^{-3}$ doped sample. This behavior implies that vacancy defects acting as positron traps are present also in these layers.

The number of different vacancy-type positron traps in the material can be studied by investigating the linearity between the valence and core annihilation parameters [11]. If only a single type of vacancy defect is present, the W parameter depends linearly on the S parameter, when the fraction η of positron annihilations at the vacancy varies: $\eta = (S - S_b)/(S_v - S_b) = (W_b - W)/(W_b - W_v)$. The inverse slope of the S-W plot is the defect specific parameter $R = (S_v - S_b)/(W_b - W_v)$. This analysis is presented in Fig. 2 by plotting the W

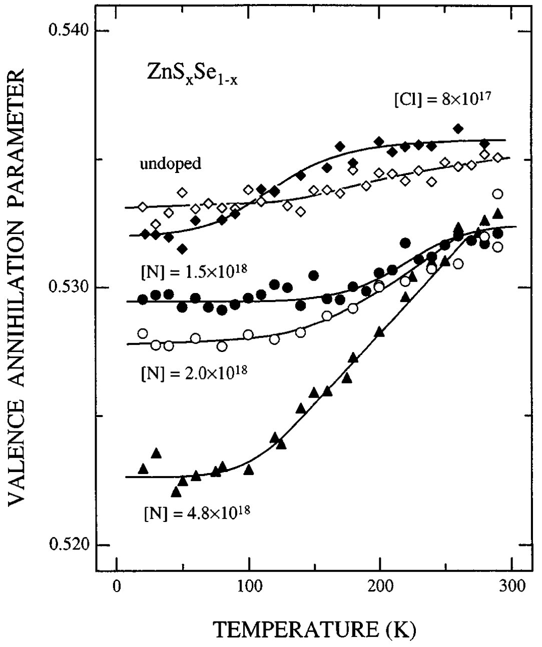

FIG. 1. The valence annihilation parameter S vs measurement temperature in various N-doped, Cl-doped, and undoped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ $(x = 0.06)$ layers. The doping concentrations of the samples are indicated in the figure. The statistical error of the S parameter is $\sigma_S = 0.0004$.

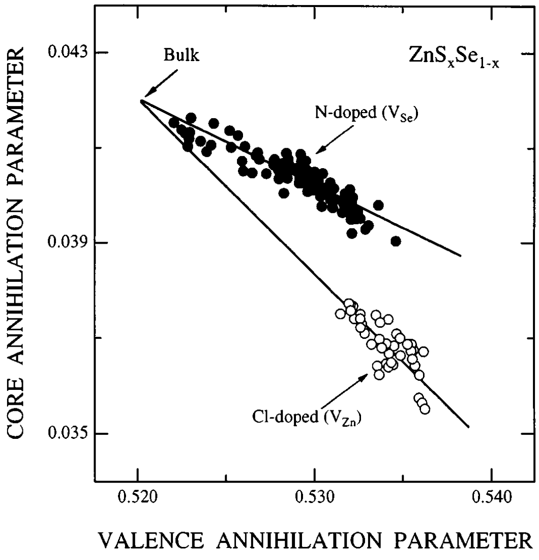

FIG. 2. The core annihilation parameter W vs the valence annihilation parameter S, measured at the same temperature, in N- and Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ $(x = 0.06)$ layers. The annihilation parameters in the defect-free $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ and the straight lines characteristic of Zn and Se vacancies are indicated. The statistical errors of the S and W parameters are $\sigma_S = 0.0004$ and $\sigma_W = 0.0002$.

parameter as a function of the S parameter measured at the same temperature.

In Fig. 2 the data in all nitrogen doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ samples form a straight line in the (S, W) plane, which indicates that a single type of vacancy explains the positron results in N-doped material. This vacancy can be characterized by the slope $R = |\Delta S/\Delta W| \approx 5$ of the solid line in Fig. 2. Similarly, the W parameter depends linearly on the S parameter in all chlorine-doped samples, implying that again a single type of vacancy, now with $R = |\Delta S/\Delta W| \approx 2.5$, is present in all of them. The vacancy in Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ is clearly different from the one observed in N-doped material.

The straight line in the (S, W) plane is formed between the end points (S_b, W_b) and $(S_{\mathrm{vi}}, W_{\mathrm{vi}})$ corresponding to the delocalized positron state in the bulk and the localized state at the vacancy i, respectively. When different types of vacancies exist in the same material, all straight lines in the (S, W) plane have the same end point at (S_b, W_b). The crossing point of the two lines in Fig. 2 determines thus the annihilation parameters of the delocalized positron in defect-free $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$: $(S_b, W_b) = (0.520, 0.042)$.

The maximum change of the annihilation parameters S and W compared to $(S_b, W_b) = (0.520, 0.042)$ gives information on the size of the detected vacancy defects. In Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ $S/S_b = 1.029$ and $W/W_b = 0.85$ at 300 K and in N-doped samples we obtain $S/S_b = 1.025$ and $W/W_b = 0.93$. We think that these values are close to the defect-specific ones $(S_{\mathrm{vi}}, W_{\mathrm{vi}})$, because they are rather independent of the doping level (see $T = 300$ K in Fig. 1). Furthermore, they are close to those observed typically for monovacancies in Si, GaAs, and InP [8]. The slopes $|\Delta S/\Delta W| \approx 2$–$5$ (Fig. 2) are also similar to those we have detected for monovacancies in GaAs and InP [8,9]. The vacancies found in N- and Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ have thus the open volume of monovacancies.

The relative amount of core electron annihilations at a vacancy defect depends on the open volume of the defect and on the chemical nature of the surrounding atoms. On the other hand, mainly the valence electrons contribute to the value of the S parameter, which thus depends predominantly on the open volume. Figure 2 shows that for the same value of S the W parameter is clearly higher for the vacancy in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ than for that in Cl-doped material. Many more positron annihilations with core electrons are thus recorded at the vacancies in N-doped than in Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. However, this difference cannot be explained by the vacancy-impurity complexes at the same sublattice: The electrons around Cl can be expected to give a larger contribution to the W parameter than those around N, leading to the opposite behavior as seen in Fig. 2.

The theoretical calculations show that in a defect-free compound semiconductor like ZnSe the largest contribution to the core annihilation rate λ_c of the delocalized positron comes from the $3d$ electrons of the Zn atoms [9]. The $3d$ shell of the Se atoms is more localized in r space and overlaps less with the positron wave function, which leads to a considerably smaller contribution to λ_c. Similarly [9], the magnitude of core electron annihilations is much larger in the Se vacancy (V_{Se}) surrounded by Zn atoms than in the Zn vacancy (V_{Zn}) surrounded by Se atoms. These arguments suggest that the vacancy defect detected in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ is the Se vacancy, whereas the one observed in Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ is the Zn vacancy.

Figure 3 shows the high-momentum part of the Doppler broadening spectrum, which was recorded at 300 K in the $[\mathrm{N}] = 1.7 \times 10^{19}$ cm^{-3} and $[\mathrm{Cl}] = 1.5 \times 10^{18}$ cm^{-3} doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ using the coincidence technique [9]. The data in the N-doped material are above those in Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ at the momentum range of $p_L = (10$–$25) \times 10^{-3}$ m_0c, indicating that the magnitude of the core electron annihilations is about 20% larger at the vacancy in N-doped than in Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. However, at the large momenta of $p_L = (25$–$40) \times 10^{-3}$ m_0c that data obtained in N-doped material fall below those recorded in Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. The two curves in Fig. 3 have different shapes: In Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ the core electron momentum distribution is clearly broader than in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$.

The broader momentum distribution indicates that the core electrons around the vacancy have higher average momentum in Cl-doped than in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. This implies that the chemical nature of the atoms surrounding the vacancy are different in the two cases. The $3d$ electrons of Zn atoms are less localized than those of Se atoms,

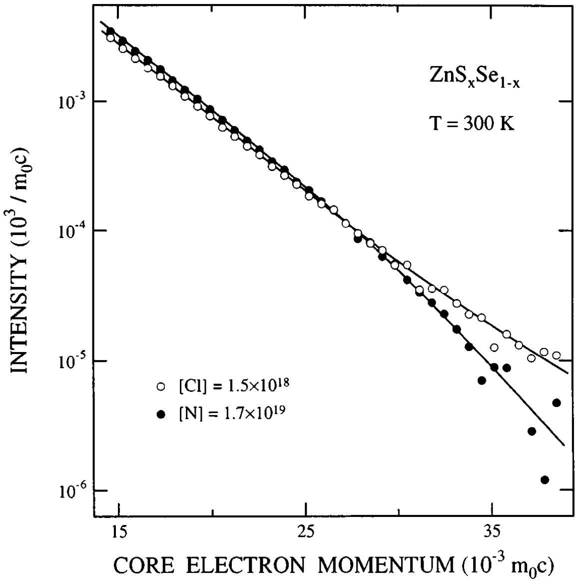

FIG. 3. The core electron momentum distribution at the vacancy defects observed in Cl-doped and N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ $(x = 0.06)$ layers. The doping concentrations of the samples are indicated in the figure.

which leads accordingly to a narrower momentum distribution. Hence the data of Fig. 3 indicate that positrons trapped at vacancies annihilate preferentially with the core electrons of Zn atoms in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ and with those of Se atoms in Cl-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. The core electron momentum distribution gives thus a direct identification of the Se vacancy in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ and the Zn vacancies in Cl-doped material.

The detection of positron trapping at Se vacancies indicates that the total charge of the observed defect is neutral or negative in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ at 300 K. On the other hand, the isolated Se vacancy in p-type ZnSe is double positive according to theoretical calculations [2]. Positive vacancies are repulsive to positrons and the isolated Se vacancy is not expected to act as a positron trap in p-type $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. The Se vacancy detected in the positron experiments must thus be a part of a complex, where the Se vacancy is closely associated with a negatively charged acceptor. The present positron data cannot be used to identify the details of this acceptor. However, such complexes as V_{Se}-N_{Se} are expected to be neutral or negatively charged for at least certain positions of the Fermi level in the energy gap [2].

The concentration of the vacancy complexes in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ can be estimated using the positron data of Fig. 1 at room temperature. The relative S parameter at monovacancies in semiconductors is typically $S_v/S_b \leq 1.03$ [8,12]. This value can be used to estimate the lower limit of the vacancy concentration, even if the exact parameter S_v/S_b is not known. The positron trapping coefficient at negative vacancies is $\mu \approx 10^{15}\ \mathrm{s}^{-1}$ [10,13], and it is roughly a factor of 2–6 less for a neutral than for a negative vacancy [13,14]. Taking $\mu = 10^{14}$–$10^{15}\ \mathrm{s}^{-1}$, we get a vacancy concentration of $[V_{\mathrm{Se}}] = 10^{18}$–$10^{19}\ \mathrm{cm}^{-3}$ in heavily N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$. This is of the same order of magnitude as the nitrogen doping concentration, thus indicating that the Se vacancy complex plays a substantial role in the electrical compensation of $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$.

Several theoretical calculations have been recently published [1–7] in order to explain the microscopic origin of the p-type doping problems in ZnSe. Garcia and Northrup have proposed that an effective compensation results from the formation of defect complexes involving the nitrogen dopant and charged native defects such as Se vacancies or Zn interstitials [2]. The present positron experiments show that a high concentration of Se vacancies is present in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ and that these vacancies are probably complexed with an acceptor defect. A most natural candidate for the acceptor is the nitrogen dopant atom. The V_{Se}-N_{Se} pair is thus a defect compatible with the observed annihilation characteristics.

In summary, we have identified the Se vacancy in N-doped $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ and the Zn vacancy in Cl-doped material by positron annihilation experiments. The total charge of the defect involving V_{Se} is neutral or negative, suggesting that the Se vacancy is in a complex with an acceptor defect, possibly with the nitrogen dopant. The concentration of Se vacancy complexes is of the same order of magnitude as the nitrogen doping concentration ($\geq 10^{18}\ \mathrm{cm}^{-3}$), indicating that the role of V_{Se} is important in the electrical compensation of p-type $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$.

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