

Atomic configurations of group V acceptors in ZnSe, ZnTe, and CdTe

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The formation of donor-acceptor pairs was detected by perturbed $\gamma\gamma$ angular correlation spectroscopy. In ZnSe, ZnTe, and CdTe crystals doped with the donor ^{111}In and one of the acceptors N, P, As, or Sb the strength of the electric field gradient shows a systematic correlation of the bond length between the respective acceptor and the neighboring cation. For N acceptors, an inward relaxation of the neighboring cations is concluded to occur. © 1996 American Institute of Physics. [S0003-6951(96)00645-6]

The highest efficiencies regarding p doping ZnSe and ZnTe are achieved using the acceptor N as the dopant.^{1,2} Decisive for the exceptional efficiency of using N was the development of molecular beam epitaxy and metalorganic chemical vapor deposition growth techniques that employ a N-plasma source. Achievable carrier concentrations, however, are still limited to about 10^{18} cm^{-3} in p -type ZnSe, which is too low for producing efficient pn junctions. In order to determine the limiting physical processes for achieving low resistive p -type conductivity, the application of locally sensitive techniques, like perturbed $\gamma\gamma$ angular correlation (PAC), is helpful. Using this technique with the donor probe ^{111}In , its interaction with the group V acceptors N, P, As, and Sb was investigated in ZnSe, ZnTe, and CdTe. The information about the group V dopants in these II-VI semiconductors was deduced from the measured electric field gradients (EFG).

The PAC technique³ is sensitive to the hyperfine interaction between an EFG and the nuclear quadrupole moment Q of a suitable radioactive probe nucleus. Since the investigated semiconductors possess a zincblende lattice, a measured EFG tensor results exclusively from defects in the vicinity of the probe atom. After the radioactive decay of the probe ^{111}In , the EFG is observed via its interaction with the electric quadrupole moment Q of an excited state of the daughter nucleus ^{111}Cd . The PAC spectrum $R(t)$ yields the interaction frequencies ω_1 , ω_2 , and ω_3 , which are proportional to the largest component V_{zz} of the EFG tensor. Usually, the traceless EFG tensor is described by the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, which is deduced from the ratio ω_2/ω_1 . The strength ν_Q of the EFG strongly depends on the distance r between the probe atom and the generating charge distribution. In case of a spherically symmetric charge distribution, the strength of the EFG decreases with r^{-3} .

Information about the group V acceptors can be obtained if a formation of close pairs takes place involving the donor ^{111}In . The formation of donor-acceptor pairs is governed by the Coulombic interaction and, therefore, depends on the existence of ionized group V acceptors. The respective EFG is measured after the transmutation of the donor ^{111}In into ^{111}Cd , which is either identical (CdTe) or isoelectronic (ZnSe, ZnTe) to the atoms of the cation sublattice. Therefore, the observed EFG is assumed to be exclusively determined by the properties of the neighboring group V acceptor.

The investigated II-VI crystals were doped with ^{111}In and the respective group V element by ion implantation.⁴ The ^{111}In atoms were implanted with an energy of 350 keV, resulting in a mean depth of about 1000 Å with a straggling of 500 Å. The respective group V elements were implanted into the same depth with a peak concentration of about 10^{19} cm^{-3} , which is significantly larger than the local ^{111}In concentration of about $4 \times 10^{16} \text{ cm}^{-3}$. Annealing of the implantation induced radiation damage was achieved by heating the crystals for 30 min under excess vapor of the respective metal component. After annealing the samples in the range $800 \leq T_A \leq 1000 \text{ K}$ (ZnSe, ZnTe) or $600 \leq T_A \leq 770 \text{ K}$ (CdTe), new, axially symmetric EFG were observed; for ZnSe, the corresponding PAC spectra are shown in Fig. 1. As Table I shows, the strength ν_Q of the measured EFG depends on the respective acceptor element and the host

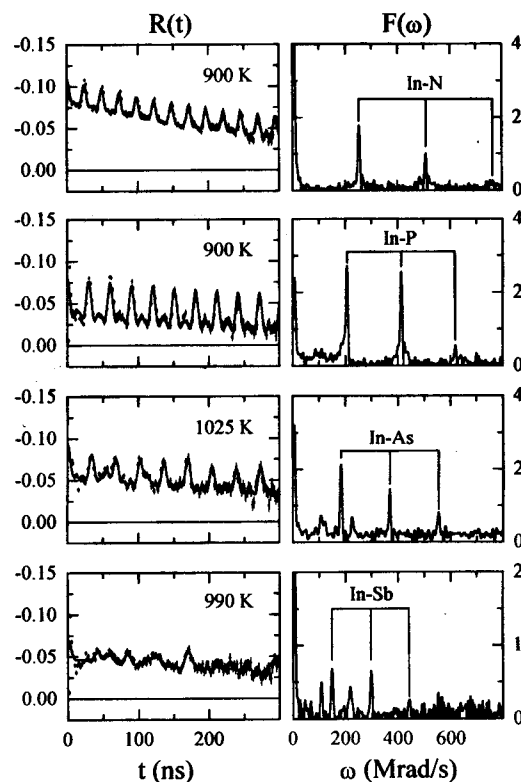


FIG. 1. PAC spectra of ZnSe, implanted with ^{111}In and the group V elements N, P, As, and Sb (top to bottom) and subsequently annealed under Zn vapor at the indicated temperatures.

TABLE I. Quadrupole coupling constants ν_Q (MHz) of ^{111}Cd -group V acceptor pairs in ZnSe, ZnTe, and CdTe, measured at 293 K; the EFG tensor is axially symmetric in all cases ($\eta=0$). The pairs were originally formed at the donor ^{111}In .

	ZnSe	ZnTe	CdTe
$^{111}\text{Cd-N}$	271(1)	262(1)	280(1)
$^{111}\text{Cd-P}$	219(2)	222(1)	212(2)
$^{111}\text{Cd-As}$	196(1)	199(1)	186(1)
$^{111}\text{Cd-Sb}$	156(1)	167(1)	153(1)

matrix.⁴ The orientation of the EFG tensor, determined for N-, As-, and Sb-doped CdTe, is along a crystallographic $\langle 111 \rangle$ axis. Strength, symmetry, and orientation of these EFG are consistent with the formation of close donor-acceptor pairs that consist of the donor ^{111}In in the cation sublattice and of the respective group V acceptor in the anion sublattice. The occurrence of an additional EFG in As- and in Sb-doped ZnSe (Fig. 1), characterized by $\nu_Q = 121$ MHz and $\nu_Q = 115$ MHz, respectively, might indicate the population of a different stable position of the respective group V acceptor close to the In atom, but will not be subject of the present discussion.

Assuming that the bond length d of a ^{111}Cd -acceptor pair is equal to the sum of the covalent radii for tetrahedral sp^3 hybridization of the respective elements,⁵ in all investigated II-VI semiconductors a linear relation between ν_Q and d^{-3} is obtained for the elements P, As, and Sb (Fig. 2). In

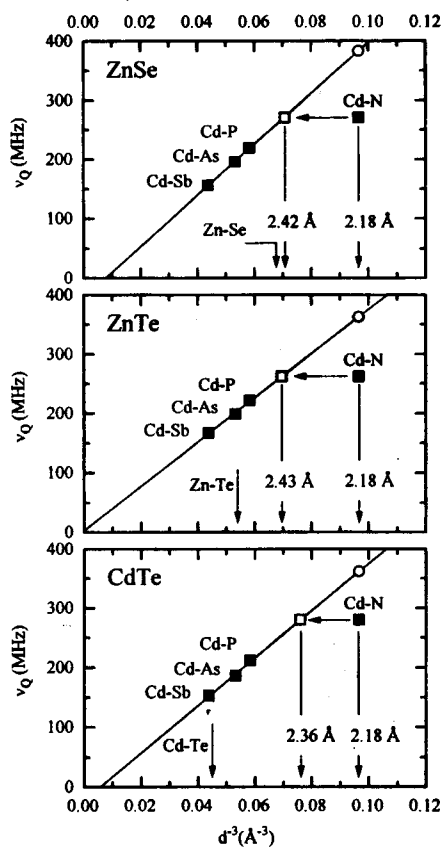


FIG. 2. Bond lengths d and EFG strengths ν_Q of ^{111}Cd -group V pairs in II-VI semiconductors. The closed squares correspond to experimental ν_Q values (see Table I) plotted as a function of the sum of the covalent radii of the involved elements.

the case of ZnSe and CdTe, the nonzero values of ν_Q , extrapolating d^{-3} to zero, can be qualitatively understood by a deviation of the distribution of the electric charge about the site of the acceptor atom from spherical symmetry.

In none of the investigated II-VI semiconductors does the Cd-N pair follow this linear relationship, if the covalent radii of Cd and N are used for calculating its bond length d (the closed squares in Fig. 2). In all cases, the measured values of ν_Q are significantly smaller than the expected ones (open circles). Assuming that the observed linear dependence also holds for Cd-N, the experimental values of ν_Q are used to extract the bond lengths of $d = 2.42, 2.43,$ and 2.36 \AA for ZnSe, ZnTe, and CdTe, respectively (open squares). These values are smaller than the bond lengths in the respective host lattices and, therefore, the deduced values for d indicate an inward relaxation of the neighboring cations toward the significantly smaller N acceptor. Since only a single EFG characterizes the Cd-N pairs in all three cases, the relaxation of N toward one of its neighboring cations, which would lead to two different EFG, is excluded.

The bond length d for Zn-N pairs in ZnSe and ZnTe were calculated by Van de Walle and Laks,⁶ yielding $d = 2.10 \text{ \AA}$ and $d = 2.11 \text{ \AA}$, respectively. Almost identical values were reported by Cheong and Chang.⁷ A comparison of these theoretical values with the experimental results obtained by PAC for the Cd-N pairs is possible, replacing Cd by Zn and correcting for the different covalent radii. With this correction, the Zn-N bond length becomes $d = 2.25 \text{ \AA}$ and 2.26 \AA for ZnSe and ZnTe, respectively, in good agreement with the theoretical values. For ZnSe doped with N, x-ray diffraction measurements showed a reduction of the lattice constant⁸ that could not be explained by the theoretically obtained shorter Zn-N bond length.⁶ The fact that the experimental results confirm the shorter bond length supports the original interpretation by Petruzzello *et al.*⁸ that the excess lattice contraction points to the generation of point defects accompanying N doping.

The systematic decrease of the coupling constants ν_Q with increasing atomic number of the involved group V elements, observed here, is in contrast to the increase of the ν_Q values with atomic number, observed for donor-acceptor pairs, formed with the acceptor ^{111}In in Si⁹ and Ge;¹⁰ these pairs were formed between the acceptor ^{111}In and different group V donors. The different systematic dependence of the EFG on the atomic numbers of the group V elements, observed in both types of semiconductors, are understandable, considering the different character of the donor-acceptor pairs formed with the ^{111}In probe. After the radioactive decay, the resulting ^{111}Cd atom is isoelectronic or identical to a host atom in the II-VI semiconductors and the local electronic charge distribution depends on the respective group V element, only. In contrast, Cd forms a double acceptor in Si and Ge and the electric charge distribution is also determined by the ionicities of the two constituents, i.e., the difference in the electronegativity between Cd and the respective group V element. In this model, the distribution of the additional charge and, thereby, the strength of the observed EFG at the site of the ^{111}Cd nucleus depends on the relative electronegativity of the group V donor and should decrease, if the electronegativity of the donor increases. That means, the

EFG of the group V- ^{111}Cd pairs in Si and Ge should increase with the atomic number of the group V element in agreement with the experimental data. Finally, it should be noted that the EFG, measured for the ^{111}Cd -group V pairs in the different II-VI semiconductors represent ideal test cases for a theoretical calculation of EFG generated by point defects, because they are mainly determined, in particular in the Cd compounds, by the nature of the respective group V element.

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