

Doping of ZnSe, ZnTe, and CdTe with Group V Elements

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Abstract

The interaction between group V acceptors and the substitutional donor In in II-VI semiconductors is studied using perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC). In ZnSe, ZnTe, and CdTe, doped by implantation or diffusion with N, P, As, or Sb, close donor-acceptor pairs are detected. Basic properties of the acceptors, such as lattice site, charge state, stability and diffusion mechanism are deduced from structure and stability of the formed pairs and from the temperature dependence of pair formation.

Introduction

The application of wide bandgap II-VI compound semiconductors as base materials for optoelectronic devices, especially in the blue wavelength region, decisively depends on the realisation of high p - and n -type conductivity in the same compound. Whereas p -type conductivity of ZnSe is limited by compensation of dopants more extensively than n -type conductivity, the problem concerning doping of ZnTe is posed vice-versa. In contrast, p - n junctions made of CdTe or HgCdTe are already realised on the device level. Recently, nitrogen produced by an RF plasma source has emerged as a rather successful dopant for p -type doping of MBE grown ZnSe layers with net acceptor concentrations as high as 10^{18} cm^{-3} [1,2]. Despite this experimental progress, some fundamental physical problems still remain unsolved. The effects leading to a limitation of carrier concentration at high N concentrations are not yet understood. Further, experiments performed so far, confirm the exceptional state of N among group V acceptors regarding its efficiency for p -doping in the case of ZnSe and ZnTe [3]. The applicability of the alternative dopants P, As or Sb, especially for the MOVPE process, would significantly reduce the technical effort for device production compared to doping during MBE growth using a N plasma. The PAC experiments presented in this paper are directed towards a systematic investigation of group V acceptors on an atomic scale, thereby representing an approach complementary to techniques like photoluminescence spectroscopy or electrical measurements, which are less sensitive to the chemical nature of the involved defect species.

Experimental Details

The PAC technique measures the defect specific electric field gradient (efg) at the site of a probe nucleus, which originates from the charge distribution around the probe atom. Since the strength of the efg decreases with the third power of the distance between probe nucleus and external charge, it is mainly determined by the immediate atomic surrounding. The radioactive probe ^{111}In decays with a half life of 2.8 days to an excited state of the daughter nucleus ^{111}Cd . From this excited state a cascade of two γ -rays is emitted, encompassing an isomeric state with a half life of 85 ns. The interaction between the quadrupole moment Q of this isomeric state and the external efg generates three frequencies ω_n in the PAC time spectrum, which is described by

$$R(t) = A_2 \left[f \cdot (S_0 + \sum_{n=1}^3 S_n \cos \omega_n t) + (1 - f) \right]. \quad (1)$$

This spectrum is deduced from the coincidence rate of the two emitted γ -rays, measured as a function of the time elapsed between the detection of both γ -rays. The components V_{ii} of the traceless efg tensor are obtained from the frequencies ω_n . The largest component V_{zz} is usually expressed by the coupling constant $v_Q = eQV_{zz}/h$, which is proportional to ω_1 . The asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ is deduced from the frequency ratio ω_2/ω_1 and satisfies the condition $0 \leq \eta \leq 1$. The coefficients S_0 and S_n depend on the orientation of the efg tensor with respect to the host lattice, i.e. the orientation of the formed defect complex. The factor f denotes the relative fraction of ^{111}In atoms that is associated with this efg, and $A_2 = -0.14$ describes the spatial anisotropy of the emission of the second γ -ray with respect to the first γ -ray. A detailed description of the PAC spectroscopy is found in [4].

For the PAC experiments presented in this paper, single crystals were doped with ^{111}In and the required group V element by ion implantation at 293 K. Additional samples were doped by diffusion of ^{111}In and As. The implantation energies and ion doses are listed in table 1 for the case of ZnSe. The values used for ZnTe and CdTe were in the same range. On the basis of the ion range distributions calculated by TRIM 87 [5] the parameters were selected to generate a sufficient overlap of the ^{111}In and the group V ion distributions. The projected range of ^{111}In ions is about 1100 Å with a straggling of 500 Å, resulting in a mean ^{111}In concentration of $4 \cdot 10^{16} \text{ cm}^{-3}$. The corresponding acceptor concentrations were in the range of 10^{19} cm^{-3} .

Table 1: Implantation parameters used for ZnSe. In the case of N, P, and As two implantations with different energies were performed.

Ion	Energy 1 (keV)	Dose 1 (cm^{-2})	Energy 2 (keV)	Dose 2 (cm^{-2})
^{111}In	350	$6.0 \cdot 10^{12}$		
^{14}N	75	$2.5 \cdot 10^{14}$	30	$1.3 \cdot 10^{14}$
^{31}P	150	$3.0 \cdot 10^{14}$	60	$1.3 \cdot 10^{14}$
^{75}As	300	$2.5 \cdot 10^{14}$	60	$0.6 \cdot 10^{14}$
^{121}Sb	350	$4.0 \cdot 10^{14}$		

In order to anneal the implantation damage and to support a substitutional incorporation of the dopants, the crystals were heated under excess metal vapour of Zn or Cd for 30 min and slowly cooled to room temperature. After each annealing step a PAC spectrum was recorded. The temperature range was 550-1100 K for ZnSe, 470-970 K for ZnTe, and 430-735 K for CdTe. Reference samples were exclusively doped with ^{111}In and treated under the same conditions. Diffusion of ^{111}In was performed for 90 min under Se or Te atmosphere at 1070 K (ZnSe and ZnTe) and at 970 K (CdTe). Additionally, As was diffused into ZnTe and CdTe under Zn and Cd vapour respectively. In the case of the acceptor P, CdTe and ZnTe were doped during crystal growth, performed by sublimation of CdTe or ZnTe bulk material at 1300 K in the presence of elemental P.

Results and Discussion

Following implantation at 293 K, the PAC spectra of the as implanted crystals were dominated by implantation damage correlated with the ^{111}In ions. As an example, the spectrum of ZnSe implanted with ^{111}In and N is shown in fig. 1. The damage is manifested on the one hand by a unresolvable distribution of efg, caused by a variety of defects at different distances in the vicinity of the probe, and results in an exponential decrease of the $R(t)$ spectrum. On the other hand, it is manifested by a unique efg ($\nu_Q = 136$ MHz, $\eta = 0.15$), which is caused by a distinct defect close to the ^{111}In probe. Defects with very similar efg parameters were detected in ZnTe ($\nu_Q = 113$ MHz, $\eta = 0$) and CdTe ($\nu_Q = 114$ MHz, $\eta = 0$) following the ^{111}In implantation. They vanish during the first annealing step at 550 K (ZnSe), 470 K (ZnTe) and 430 K (CdTe), which indicates the low thermal stability of these complexes. The efg observed in CdTe has been attributed by Wegner and Meyer [6] to an unstable $\text{In}_{\text{Cd}}\text{-V}_{\text{Te}}$ complex consisting of two donor species. Therefore, the formation of analogous $\text{In}_{\text{Zn}}\text{-V}_{\text{Te}}$ and $\text{In}_{\text{Zn}}\text{-V}_{\text{Se}}$ complexes is assumed for ZnTe and ZnSe because of the similarity in the strength of the efg and the low thermal stability of the formed pairs.

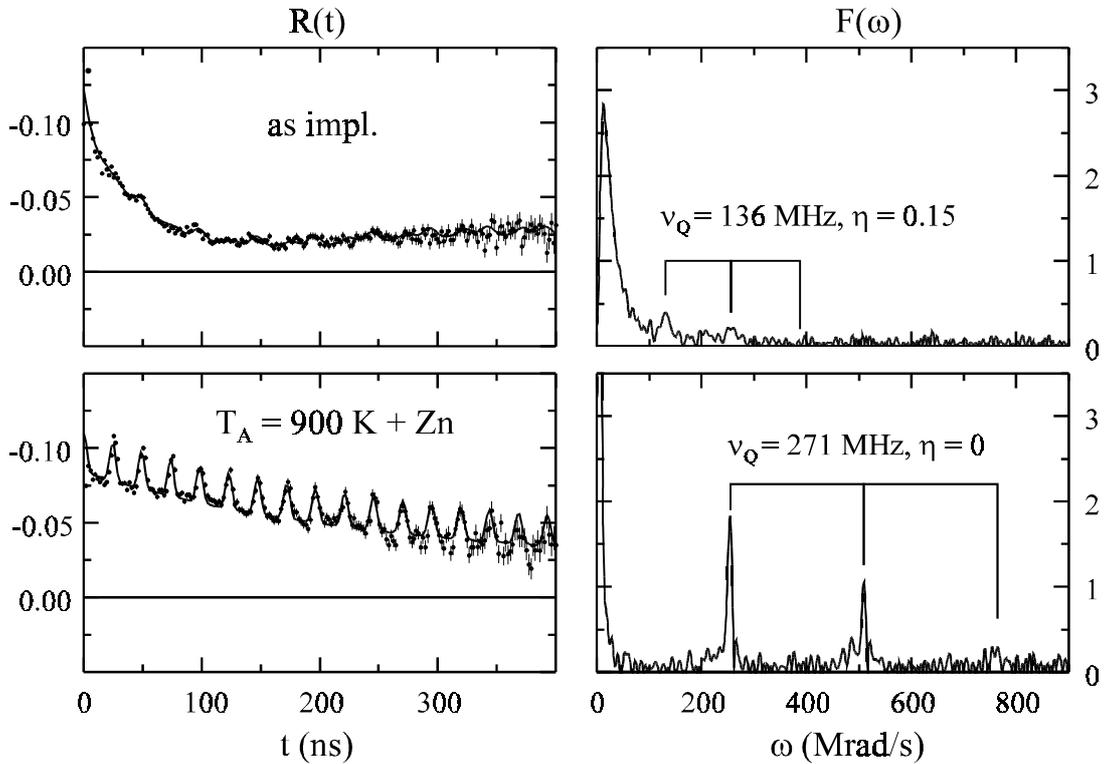


Figure 1: PAC spectra of ZnSe doped with ^{111}In and N by implantation at 293 K (top) and annealed under Zn overpressure at 900 K (bottom).

During annealing at increasing temperatures, the damage, induced by the implantation process, disappeared successively, depending on the respective compound and the implanted co-dopant. The fraction of ^{111}In probes remaining in a damaged lattice environment increased with the mass of the implanted acceptor ions, ranging from 14 % for ZnSe:In+N to 50 % for ZnSe:In+Sb after annealing at 1000 K.

The interaction between the donor ^{111}In and the different acceptors is discussed in detail for ZnSe:In+N. The effect of co-doping with N became visible at annealing temperatures, sufficiently

high to mobilise the N atoms, so that their incorporation on a substitutional lattice site as negative ions can occur. Following annealing at 900 K, an axially symmetric efg with $\nu_Q = 271$ MHz was detected, which is exclusively observed in ZnSe doped with N (fig. 1). The strength of the N specific efg, e.g. in comparison with that of the cation vacancy ($\nu_Q = 72$ MHz, $\eta = 0.05$) [7], and the axial symmetry of the efg indicate that the detected defect complex is an $\text{In}_{\text{Zn}}-\text{N}_{\text{Se}}^-$ donor-acceptor pair, which is formed by trapping of N_{Se}^- at In_{Zn}^+ due to Coulomb interaction. Analogous pairs were observed in ZnSe doped with P, As, or Sb. All complexes are characterised by an axially symmetric efg tensor ($\eta = 0$) with a strength (ν_Q) that is unambiguously connected to the respective group V acceptor element. The experiments on ZnTe and CdTe demonstrate that donor-acceptor pair formation is common to all three compounds (table 2). The strength of the pair-specific efg is mainly determined by the respective element, acting as the acceptor, and to a lower extent by the respective matrix. In the case of CdTe:In+As and CdTe:In+Sb, the orientation of the efg was measured to be along the $\langle 111 \rangle$ -crystal axis. Annealing under chalcogen vapour at 900 K (ZnSe) and 700 K (CdTe) was performed at ZnSe:In+P and CdTe:In+As crystals, which previously had been annealed at the same temperature under addition of the respective metal component. The result was an irreversible dissolution of the donor-acceptor pairs, which indicates that chalcogen atoms replaced P or As atoms.

Table 2: Coupling constants ν_Q [MHz] of ^{111}In - group V acceptor pairs in II-VI compounds. The efg tensors are axially symmetric ($\eta = 0$). Complexes marked with d were also observed in diffused crystals. Index s denotes doping during crystal growth by sublimation.

Matrix \ Dopant	ZnSe	ZnTe	CdTe
N	271 (1)	262 (1)	
P	219 (2)	222 (1) ^s	212 (1) ^s
As	196 (1) ^d	199 (1)	186 (1) ^d
Sb	156 (1)		153 (1)

A second efg, belonging to a smaller fraction of In probes, was observed in ZnSe:In+As ($\nu_Q = 122$ MHz, $\eta = 0.1$) and in ZnSe:In+Sb ($\nu_Q = 115$ MHz, $\eta = 0$). Because of the nearly axial

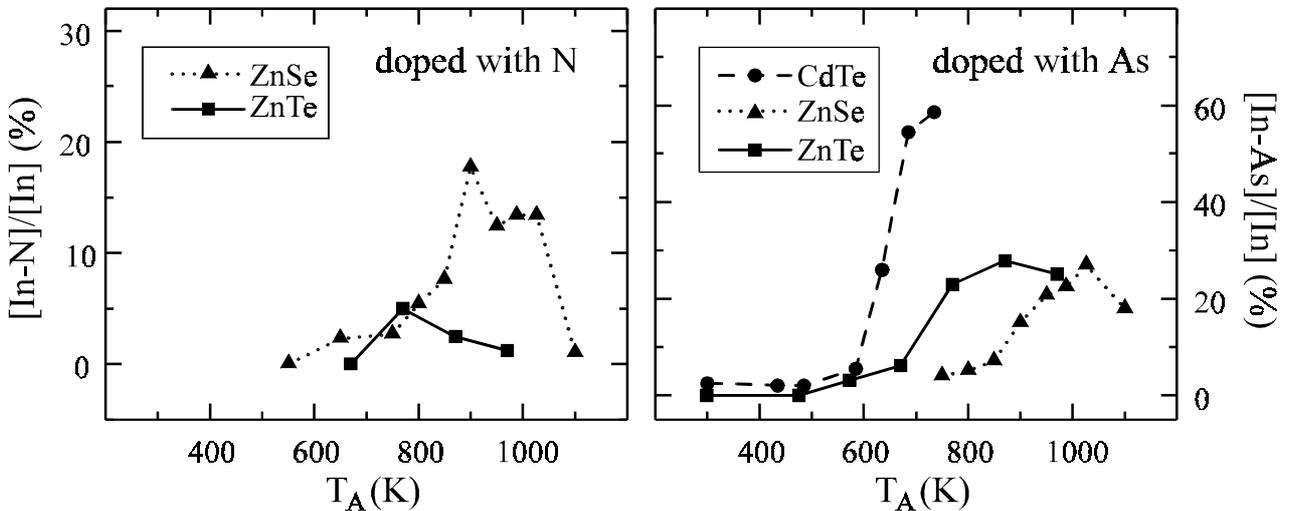


Figure 2: Temperature dependence of the fraction f (see eq. 1) of ^{111}In atoms, forming donor-acceptor pairs during annealing of implanted samples.

symmetry, these efg might be caused by a relaxation of As and Sb along a $\langle 111 \rangle$ lattice direction.

The fraction f of In atoms that form pairs, increases with the annealing temperature, reaches a maximum and finally decreases due to dissolution of pairs (fig. 2). These fractions show that the temperatures that are necessary to mobilise the acceptor impurities and to incorporate them on substitutional sites, primarily depend on the matrix and secondly on the group V element. In particular for the case of As, the temperatures required for observing significant pair formation ($f = 5\%$), being 600 K for CdTe, 670 K for ZnTe, and 800 K for ZnSe, correlate with the respective melting temperatures of 1362 K, 1512 K, and 1793 K, respectively.

Relaxation of the crystal lattice around acceptors in II-VI compounds can change their electronic levels in the bandgap [8] and the elastic energy, which contributes to the energy needed to form a substitutional acceptor. Therefore, a more detailed analysis of the lattice structure around the acceptors is necessary, which should be possible because the efg is sensitive to the distance d between the ^{111}In donor and the respective group V acceptor. If d is assumed to be determined by the sum of the covalent radii of the probe ^{111}Cd and the respective acceptor element, a linear relation between ν_Q and d^{-3} is obtained for P, As, and Sb in ZnSe. The covalent radii of these elements are larger than that of Se. In contrast, the radius N of is significantly smaller and it is plausible to expect that the ν_Q value for N should deviate from this linear relation due to a reduced Zn-N bond length.

Summary and Outlook

Because the pairing of group V acceptors with ^{111}In donors results in well-defined efg tensors, PAC is suited to identify these elements as impurities in II-VI compounds. Such a contamination can originate, for example, from III-V substrates, used for the heteroepitaxy of II-VI epilayers or from the interface of p - n junctions. Self compensation at high nitrogen doping levels will be examined in future experiments with help of the acceptor probe ^{79}Rb , which is supposed to interact with compensating donors. Further information concerning the atomic configuration of N in ZnSe should be obtained with help of the probe atom ^{77}Br , which acts as a donor in the chalcogen sublattice. First experiments in ZnSe indicate that implanted ^{77}Br and N form donor-acceptor pairs with an interaction weaker than that of In-N pairs due to the larger donor-acceptor distance.

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