Generation of intrinsic defects in CdS : In by doping with Li atoms

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CdS crystals were doped with In and Li atoms in order to study the behaviour of Li in this II–VI compound semiconductor. By the perturbed angular correlation technique (PAC), using ^{111}In as radioactive donor atom, Li doping at 800 K was observed to lead to a pronounced formation of In_{Cd}–V_{Cd} pairs. A formation of In_{Cd}–Li_{Cd} pairs, however, was not detected in spite of the fact that Li is reported to exist as Li_{Cd} in CdS thereby acting as an acceptor atom. The Li induced formation of In_{Cd}–V_{Cd} pairs was investigated under different experimental conditions including isochronal annealing programs.

1. Introduction

In the past, the perturbed angular correlation technique (PAC) has been successfully applied for the study of defects in semiconductors [1]. Using radioactive atoms as dopants predominantly the interaction between donor and acceptor atoms has been investigated. With regard to II–VI semiconductors, however, little information is available; there are some studies on ^{111}In doped ZnO [2], CdTe [3,4], and CdS [5–7].

The aim of the here discussed PAC experiments is to contribute to a microscopic understanding of the rather problematic p-type conductivity in II–VI compounds. A good candidate to achieve p-type conductivity is the element Li which, based on photoluminescence experiments, is reported to occupy the Cd site in CdS thereby acting as an acceptor atom [8]. In order to examine a potential formation of donor–acceptor pairs between In_{Cd} and Li_{Cd} atoms, CdS crystals diffused with ^{111}In and Li atoms were analyzed using the PAC technique.

2. Experimental method

The PAC technique uses the defect specific electric field gradient (EFG) which at a particular lattice site is determined by the local electrical charge distribution. Working with the radioactive probe atom ^{111}In, which decays with a half-life of 2.8 d to its daughter isotope [111]Cd, the EFG will generate three frequencies in a PAC time spectrum $R(t)$. From a least-squares-fit to this spectrum the different components V_{ii} of the EFG tensor are obtained via the coupling constant $\nu_Q = eQV_{zz}/h$ (Q is the nuclear quadrupole moment) and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ ($0 \leqslant \eta$

$\leqslant 1$). A more detailed description of the PAC method can be found e.g. in ref. [1].

3. Results

3.1. Formation of ^{111}In-defect complexes

In order to look for a potential formation of complexes formed between the donor atom ^{111}In and the acceptor atom Li, CdS single crystals (typically 5 to 10 mm³, Eagle Picher) were first diffused inside an evacuated quartz ampoule with the radioactive ^{111}In atoms (1073 K, 90 min, 3 bar S_2 overpressure). The samples were cooled by fast immersion of the closed quartz ampoule into water (vacuum quench). The formed In_{Cd}–V_{Cd} pairs, known to occur after this procedure [6], were subsequently annealed for 20 min at 874 K (compare fig. 4, top) so that the ^{111}In atoms were incorporated at unperturbed Cd sites of the hexagonal CdS lattice characterized by $\nu_Q = 7.4$ MHz and $\eta = 0$. In the second step, the crystals were diffused with Li (793 K, 30 min); the resulting PAC time spectrum $R(t)$ along with its Fourier transform $F(\omega)$ is shown in fig. 1 (top). Obviously, the lattice EFG with $\nu_Q = 7.4$ MHz (corresponding to ω values around 10 Mrad s⁻¹) is no longer visible and more than 80% of the ^{111}In atoms have formed In_{Cd}–V_{Cd} pairs that are recognized by their known EFGs described by $\nu_{Q2} = 72.4$ MHz, $\eta = 0.35$ and $\nu_{Q3} = 78.7$ MHz, $\eta = 0.21$ [6]. For comparison, fig. 1 (bottom) shows the PAC spectrum measured at a CdS crystal directly after doping with ^{111}In under S_2 overpressure (1073 K, 90 min); here, also the EFG characterizing In_{Cd} in an unperturbed environment is visible. The identical frequencies (ν_{Q2} and ν_{Q3}) observed in both experiments prove that diffusion of CdS
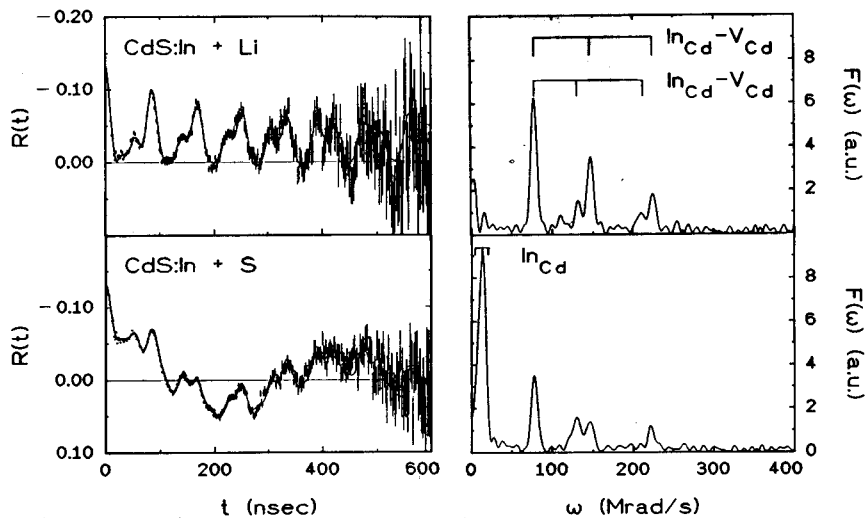
Fig. 1. PAC time spectra $R(t)$ (left) and their Fourier transformations $F(\omega)$ (right) showing the formation of $In_{Cd}-V_{Cd}$ pairs in CdS after Li diffusion at 793 K (top) and after firing under S_2 at 1073 K (bottom). The ratios of the amplitudes in the Fourier transforms are different in both experiments because the orientation of the single crystal was randomized for recording the upper spectrum.

with Li generates the same $In_{Cd}-V_{Cd}$ pairs that are found after firing CdS under S_2 overpressure. It is remarkable that the treatment of the sample with Li at only 793 K produces twice as much $In_{Cd}-V_{Cd}$ pairs, yielding the fractions $f_2 = 40\%$ and $f_3 = 42\%$, as firing under S_2 at 1073 K, yielding $f_2 = 18\%$ and $f_3 = 21\%$. Because of the absence of a new EFG after Li diffusion of CdS in all experiments, however, it is shown that there is no pairing between the donor In and Li atoms within the experimental sensitivity of the present PAC experiments ($f < 2\%$).

The high efficiency of Li of introducing V_{Cd} defects into CdS is also visible in fig. 2 which compares the diffusion of CdS with ^{111}In in a sulfur (top) and in a Li atmosphere (bottom) at 790 K (90 min). Under both conditions, the fraction of incorporated ^{111}In is considerably reduced compared with the diffusion at 1073 K, but in the case of sulfur only 20% of ^{111}In atoms are incorporated at well defined Cd lattice sites whereas in the case of Li 77% of ^{111}In atoms are incorporated as $In_{Cd}-V_{Cd}$ pairs.

It might be questioned whether the defect frequencies ν_{Q2} and ν_{Q3} are really caused by a trapped V_{Cd} or whether they are actually caused by a trapped Li_{Cd} acceptor. Without repeating the arguments given in ref. [6], one would have to assume that firing CdS at high temperatures, without intentional doping with Li, generates $In_{Cd}-Li_{Cd}$ pairs. This assumption receives support by a report of Henry et al. [8] who claim that pure CdS crystals contain about 2×10^{15} Li cm^{-3} as a contamination. In order to verify this possibility a CdS crystal was diffused with a mixture of radioactive ^{111}In

and stable In (1073 K, 90 min S_2 overpressure). From the fact that 95% of the radioactive ^{111}In was incorporated a lower limit for the average In concentration of 10^{18} In cm^{-3} was estimated assuming a homogeneous In distribution across the sample; obviously, the local In concentration can exceed this value. The corresponding PAC spectrum in fig. 3 yields 50% of $In_{Cd}-$defect pairs requiring a Li concentration of at least 5×10^{17} cm^{-3}. Since this value is by a factor of 100 higher than the above mentioned Li contamination an
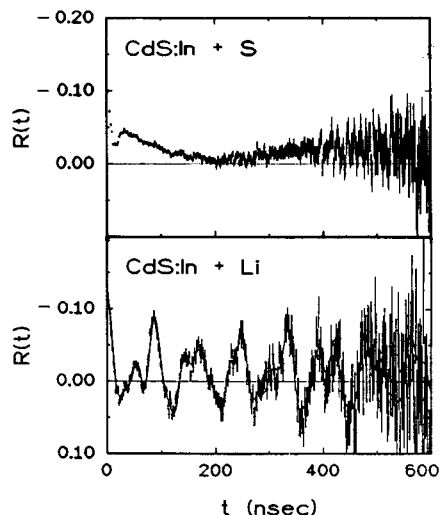

Fig. 2. PAC spectrum measured after diffusion of CdS with ^{111}In at 790 K in the presence of sulfur (top) and in the presence of Li (bottom).
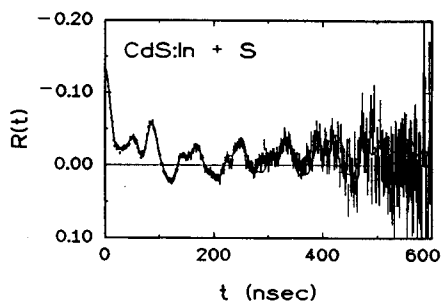
Fig. 3. Formation of $In_{Cd}-V_{Cd}$ pairs in CdS after diffusion at 1073 K under S_2 overpressure with an amount of In that corresponds to a concentration of 10^{18} In cm^{-3}.

explanation of both observed defect EFG in terms of trapped Li atoms is excluded and the original assignment as an $In_{Cd}-V_{Cd}$ complex is confirmed.

3.2. Thermal stability

For a better understanding of the formation conditions of the $In_{Cd}-V_{Cd}$ pairs fig. 4 shows the results of PAC experiments at 295 K obtained after heating of CdS crystals for 10 min at different temperatures T_A. The open and closed symbols refer to annealing in an open system under normal pressure conditions (air) and inside a closed evacuated quartz ampoule, respectively; the cooling rate of the crystal can be assumed to be lower in the latter case.

For the CdS crystals fired under S_2 (fig. 4, top), a gradual decrease of the $In_{Cd}-V_{Cd}$ pairs with tempera-

Fig. 4. Influence of isochronal annealing (10 min) of CdS on the fraction of $In_{Cd}-V_{Cd}$ pairs recorded at 295 K. The open square corresponds to a second annealing for 30 min at 800 K.

ture until their almost disappearance around 800 K is observed. Since the fraction of ^{111}In atoms on unperturbed Cd lattice sites increases at the same time this decrease means a dissociation of the pairs into their constituents ^{111}In and V_{Cd}. The decrease of the pairs over the large temperature range of 400 K indicates that no simple dissociation reaction takes place but that as an additional process a renewed formation of the pairs occurs during cooling down. This process seems to be suppressed by the higher cooling rate that is reduced in case of the evacuated quartz ampoule (closed symbols) and which is inherently also varied during the annealing sequence. Around 800 K and above, thermally created V_{Cd} defects lead to an increase in the fraction of $In_{Cd}-V_{Cd}$ as is visible by a slowing down of the rate of decrease of the pair fraction with temperature and by the increase of the fraction at 800 K if the crystal is annealed for a time longer than 30 min (open square). In the case of the Li diffused samples (800 K), the dependence of the fraction of $In_{Cd}-V_{Cd}$ pairs on temperature is similar if annealing is performed in an open system (open symbols in fig. 4, bottom). The same holds for annealing in the closed system up to about 500 K. Beyond 600 K, however, an increase of the pair fraction occurs followed by a much slower decrease up to 800 K. Obviously, annealing in the closed ampoule prevents the irreversible loss of Li from the crystal which seems to happen around 500 K, and thereby stabilizes the higher, Li induced V_{Cd} concentration.

4. Discussion

The PAC experiments have shown that doping of CdS with In and Li atoms does not lead to a formation of $In_{Cd}-Li_{Cd}$ pairs but, instead, effects a pronounced formation of $In_{Cd}-V_{Cd}$ pairs; these pairs correspond to the self-compensating metal vacancy–donor associates in ZnS and ZnSe detected by ESR [9]. Both observations are understandable if the following transformation of the acceptor Li_{Cd}, at least at 800 K, is assumed

$$Li_{Cd}^- \rightarrow Li_i^+ + V_{Cd}^{2-}. \tag{1}$$

Then, i) no pairing between the donor In_{Cd} and the donor Li_i will take longer place; ii) a very high probability for pairing between In_{Cd} and V_{Cd} defects, created to compensate the donor Li_i, will exist. In such a model, both the group-III element In and the group-I element Li are self-compensated by the same V_{Cd} defect, and, contrary to the literature [8], p-type CdS is caused by a Li_i-V_{Cd} complex rather than by the Li_{Cd} atom. For Li in ZnSe, the transition shown in eq. (1) was also proposed by Oguchi et al. based on electronic structure calculations in the local-density-functional formalism [10].
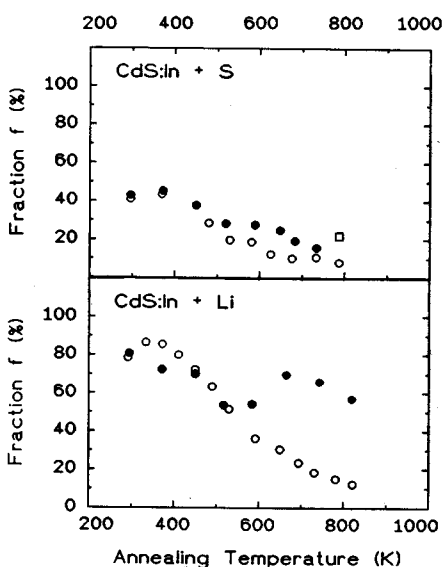
Whether at room temperature Li in CdS remains at this interstitial site is not clear at this time. It can be excluded, however, that Li occupies a V_{Cd} defect that is trapped by an In_{Cd} atom in order to form Li_{Cd} because the corresponding new EFG is not visible. However, a different Li site at room temperature might be indicated by the dip in the annealing curve (full circles) of fig. 4 (bottom): If it is assumed that below 600 K Li occupies a lattice site different from Li_i, possibly Li_{Cd}, no extra V_{Cd} defects would be stabilized because of the absence of Li_i and the annealing sequence should proceed as for the In_{Cd}–V_{Cd} pairs in samples that were not doped with Li (see fig. 4, top). At 600 K, the transition described by eq. (1) takes place producing again extra V_{Cd} and causing the observed growth of the In_{Cd}–V_{Cd} fraction. Because of the importance of Li for the doping of II–VI semiconductors similar studies in the other II–VI materials are in progress.

Acknowledgement

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