

THE INCORPORATION AND COMPLEX FORMATION OF Ag ACCEPTORS IN CdTe

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ABSTRACT

Using the radioactive isotope ^{111}Ag , the incorporation of Ag into CdTe is investigated by photoluminescence spectroscopy (PL) and the perturbed $\gamma\gamma$ -angular correlation technique (PAC). PL is used to demonstrate the incorporation as a substitutional acceptor (Ag_{Cd}) by monitoring the intensity of the donor-acceptor transition, corresponding to an acceptor level of $E_{\text{V}} + 108 \text{ meV}$, which decreases just with the half life of the radioactive decay of the ^{111}Ag isotope. Since the isotope ^{111}Ag also serves as a probe atom for PAC experiments, it is possible to confirm the incorporation of Ag atoms on lattice sites with cubic symmetry. Additionally, in CdTe a defect complex is detected, which is assigned to a $\text{Ag}_{\text{Cd}}\text{-V}_{\text{Te}}$ pair. A second defect complex is observed in CdTe doped with In, which is assigned to an $\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$ pair. By PAC experiments with the probe ^{111}In that are performed in Ag doped CdTe, the formation of the $\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$ pair is confirmed besides the well known formation of the $\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pair. The migration energy of the cation vacancy is estimated on the basis of an isothermal annealing sequence.

INTRODUCTION

The group I element Ag is a potential acceptor in CdTe if it is incorporated substitutionally on a Cd-site. The p-type conductivity of CdTe upon doping with Ag, however, is limited to a hole concentration of $2 \times 10^{16} \text{ cm}^{-3}$ [1] although a much higher concentration of Ag atoms can be introduced. The failure of a more effective p-type doping with Ag acceptors may be due to either compensating intrinsic defects or to the incorporation of Ag at interstitial lattice sites. Thus, it was proposed by Chamonal et al. and by Monemar et al. [2,3] that close pairs of substitutional Ag_{Cd} acceptors and Ag_{i} donors are formed, which are no longer electrically active.

EXPERIMENT

Radioactive ^{111}Ag atoms were implanted into CdTe crystals at the mass separator ISOLDE (CERN). The typical dose was $1 \text{ to } 5 \times 10^{13} \text{ cm}^{-2}$ and the energy was 60 keV. The resulting local concentration of ^{111}Ag atoms after implantation was estimated to 10^{19} cm^{-3} at a depth of 27 nm below the surface. The radiation damage was subsequently annealed at temperatures between 500 K and 700 K either under vacuum conditions or under Cd vapour. The intensity of the β -radiation of the ^{111}Ag decay was measured before and after annealing at the implanted (front) side and at the back side of the crystal. While after implantation the β -radiation could be detected only at the front of the crystal, after subsequent annealing the β -intensity became nearly equal on both sides. It is concluded that after annealing the majority of ^{111}Ag is distributed over the entire crystal with a thickness of 0.5 mm, resulting in a concentration of $10^{14} - 10^{15} \text{ cm}^{-3}$ Ag atoms within the crystal, if a homogeneous distribution of the Ag atoms is assumed.

The CdTe crystals used for the photoluminescence (PL) investigations were pre-treated as described elsewhere [4]. After implantation of the ^{111}Ag ions, the crystals were annealed at 620 K for 30 min under vacuum conditions. The PL spectra were recorded at 1.8 K using the 638.2 nm line of a He-Ne Laser. The luminescence was analysed by an 0.5 m grating monochromator using a CCD camera.

The PAC experiments with the probe ^{111}Ag , which was employed for the characterisation of semiconductors for the first time, complements the PAC experiments using the more readily available probe ^{111}In [5]. Both isotopes decay to the daughter isotope ^{111}Cd , which is a host atom in CdTe, while the parent isotopes act either as acceptors (^{111}Ag) or as donors (^{111}In). The employment of both isotopes, therefore, gives access to both, donor-like and acceptor-like defects, which are attracted to the radioactive probe atoms by the Coulomb interaction. While the ^{111}Ag atoms were incorporated into CdTe by implantation, as described above, the ^{111}In atoms were incorporated by diffusion at 970 K for 90 min. The concentration of ^{111}In atoms was estimated to about 10^{16} cm^{-3} within a layer of about $1\ \mu\text{m}$ below the surface. The PAC investigations at CdTe using the probe ^{111}Ag were performed either at undoped bulk crystals or at In doped MOCVD grown layers. For the PAC experiments using the probe ^{111}In , the CdTe crystals were additionally doped with stable Ag. A layer of 10 nm Ag metal was evaporated onto the surface of a bulk crystal with a thickness of 0.5 mm that was previously doped with ^{111}In . Subsequently, the Ag atoms were diffused into the crystal at 550 K for 30 min. Assuming a homogeneous distribution of the Ag atoms within the crystal, the Ag concentration was estimated to be $5 \times 10^{17}\text{ cm}^{-3}$. This assumption is based on the high diffusion coefficient of Ag in CdTe, which is reported to be $10^{-8}\text{ cm}^2/\text{s}$ at 300 K [6].

The PAC technique detects the hyperfine interaction between the quadrupole moment Q of the nucleus of the probe atom with an external electric field gradient (EFG). Following the radioactive decay, for both probe atoms ^{111}Ag and ^{111}In the hyperfine interaction takes place at the same excited $I = 5/2$ level of ^{111}Cd . Since the cubic lattice structure of CdTe causes a zero EFG at substitutional lattice sites, a non-zero EFG points to the presence of an intrinsic or extrinsic defect. The hyperfine interaction causes a modulation of the PAC time spectrum $R(t)$, which is governed by three frequencies ω_1 , ω_2 , and $\omega_3 = \omega_1 + \omega_2$. From these modulation frequencies the EFG tensor is deduced, which is described by the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. The amplitude of the modulation yields the fraction of probe atoms, which are included in the defect complex characterised by ν_Q and η . The PAC technique is mainly sensitive to defects localised close to the radioactive probe atom because the strength of the quadrupole interaction decreases strongly with the distance to the defect. A detailed description of the PAC spectroscopy in semiconductors can be found in the literature [7].

RESULTS

PL investigations at CdTe crystals doped with radioactive ^{111}Ag

The application of PL spectroscopy to semiconductors that are doped with radioactive donors or acceptors allows the unambiguous identification of the chemical nature of impurities causing a particular PL signal [8]. Assuming that the intensity of a PL signal is proportional to the concentration of the corresponding impurity atom, the intensity of this signal will change as a function of time, if the concentration of the responsible impurity changes due to its radioactive

decay. The identification of the chemical nature of impurities by PL using radioactive isotopes was first performed in the case of the Cu acceptor in ZnS [9]. It should be noted that the PL intensity is not always proportional to the impurity concentration as was shown by Magerle et al. in case of ^{111}In in GaAs [10]. In this case deviations from the proportionality were observed, which are explained by the high concentration of inhomogeneously distributed radioactive impurity atoms.

In CdTe, the acceptor responsible for a donor-acceptor transition (DAP) at 1.491 eV ($\lambda = 831.6$ nm) corresponds to an energy level of $E_V + 108$ meV and was assigned by Chamonal et al. to the Ag_{Cd} acceptor [1,11]. The assignment is based on the enhanced intensity of the DAP transition upon diffusion of Ag. This assignment, however, is not conclusive because also intrinsic defects, which are generated during the diffusion process, might be responsible for the PL signal at 1.491 eV. It was reported that at ambient temperature the intensity of this DAP transition decreases slowly with time, characterised by a time constant of 15 d. Also this aging effect could be explained by intrinsic defects generated during the diffusion process.

For the verification of the assignment of the 108 meV level, PL investigations were performed using the radioactive isotope ^{111}Ag . PL spectra were taken over a time period of 47 days, during which the sample temperature was kept below 150 K in order to exclude the aging effects observed by Chamonal et al. After implantation and subsequent annealing a DAP transition at 1.491 eV was observed, that decreased in intensity as a function of time and was not detectable anymore after 47 days (fig. 1a). The quantitative analysis of the course of the intensity yields a half life of 7.2 (4) d, which is in very good agreement with the half life of the radioactive decay of the ^{111}Ag isotope of 7.45 days (fig. 1b). This agreement shows that the 108 meV level corresponds to an acceptor, which contains a single Ag atom, and confirms the earlier assignment to the substitutional Ag_{Cd} acceptor. A more detailed description of this experiment can be found in [12].

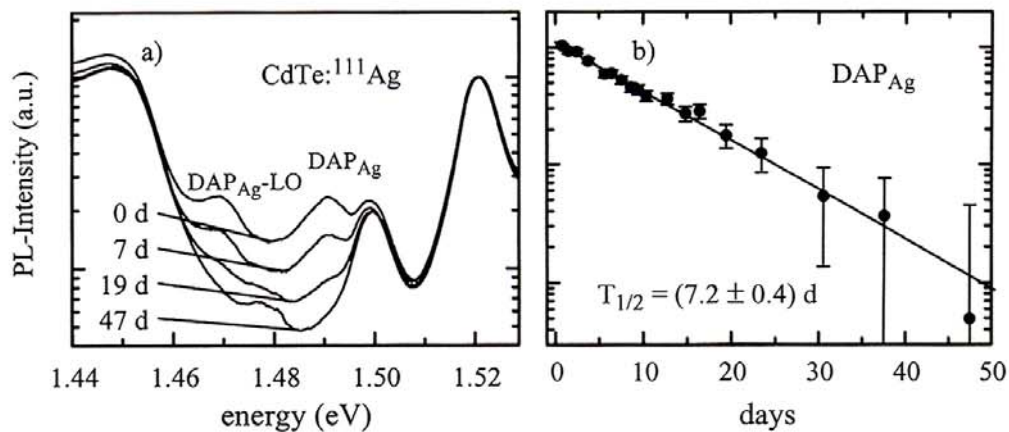


Fig. 1: PL intensity of the DAP signal assigned to the Ag acceptor. (a) PL spectra in the region of the DAP line and (b) the integrated intensity of the DAP signal as a function of the time passed after implantation.

PAC experiments using ^{111}Ag

The incorporation of Ag atoms into CdTe was investigated by PAC using the probe ^{111}Ag . In a MOCVD grown CdTe layer, which was doped with In donors during growth, after implantation of ^{111}Ag and subsequent annealing at 650 K under Te pressure, about 65 % of the Ag atoms are observed on lattices sites with cubic symmetry. The observed cubic symmetry is consistent with the incorporation of Ag atoms as acceptors on Cd-sites and, therefore, with the interpretation of the PL data discussed above. Additionally, the formation of a defect complex is observed, which is characterised by $\nu_Q = 62 \text{ MHz}$ and $\eta = 0$ (fig. 2a). The defect complex disappears after thermal treatment of the sample under Cd pressure at 650 K. The influence of the respective annealing ambient, Te or Cd vapour, on the observed increase and decrease of the concentration of this defect complex can not be explained by the interaction of Ag acceptors with the intrinsic, donor-like point defects V_{Te}^+ or Cd_i^- . In this case just the opposite behaviour regarding the formation and dissociation conditions would be expected. The fact that the defect complex was observed only in In doped CdTe rather points to the formation of $\text{Ag}_{\text{Cd}}\text{-In}_{\text{Cd}}$ pairs.

In a bulk crystal, implanted with ^{111}Ag and subsequently annealed at 550 K for 30 min in vacuum, about 50 % of the Ag atoms are observed on lattice sites with cubic symmetry. After subsequent diffusion of In into the CdTe crystal at 800 K, a fraction of 10 % of the Ag atoms formed a defect complex with an axially symmetric EFG ($\eta = 0$) that, now, is characterised by $\nu_Q = 132 \text{ MHz}$. The fraction of Ag atoms forming this defect complex is increased to 45 % after an additional thermal treatment at 800 K under Cd pressure for 30 min (fig. 2b) and vanishes after heating the crystal at the same temperature (60 min) under Te pressure. The measured orientation of the EFG tensor is in agreement with a z-axis being parallel to $\langle 111 \rangle$ lattice directions and suggests a defect complex consisting of the radioactive $^{111}\text{Ag}_{\text{Cd}}$ acceptor and a donor defect on the nearest Te-site. The occurrence of the defect complex after the thermal treatment under Cd pressure is of special importance and points to the formation of the donor-like Te vacancy. Therefore, the defect complex is assigned to the close $^{111}\text{Ag}_{\text{Cd}}\text{-}V_{\text{Te}}$ pair, which also explains symmetry and orientation of the observed EFG tensor. The observed EFG could, in principle, also be explained by the interstitial donor Ag_i trapped at the anti-bonding site with respect to the Ag_{Cd} acceptor, forming a $\text{Ag}_i\text{-Ag}_{\text{Cd}}$ pair, as was proposed by Chamonal et al. and Monemar et al. [2,3]. For such a pair, however, two significantly different EFG are expected because of the two different possible sites of the probe ^{111}Ag in such a pair, i.e. $^{111}\text{Ag}_i\text{-Ag}_{\text{Cd}}$ and $\text{Ag}_i\text{-}^{111}\text{Ag}_{\text{Cd}}$. Therefore, the assignment to a $\text{Ag}_i\text{-Ag}_{\text{Cd}}$ pair is excluded.

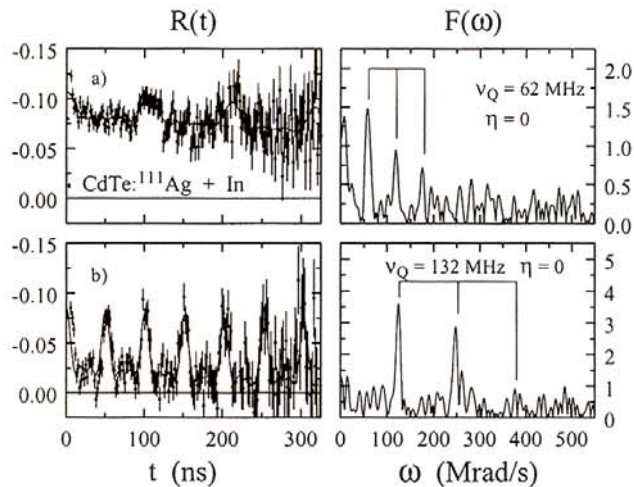


Fig. 2: PAC spectra measured with the probe ^{111}Ag in CdTe: (a) MOCVD grown, In doped CdTe after annealing at 650 K under Te pressure and (b) bulk material (In doped) after annealing under Cd pressure at 800 K.

PAC experiments using ^{111}In

In a CdTe crystal doped with ^{111}In , about 45 % of the In atoms are observed to be located at substitutional Cd-sites, as indicated by a zero EFG. After subsequent Ag diffusion, the PAC spectrum recorded at 295 K yields two, slightly different EFG characterised by $\nu_Q = 60.7(5)$ MHz, $\eta = 0.18$ and $\nu_Q = 56.6(5)$ MHz, $\eta = 0.11$ (fig. 3a). The first defect complex is known from earlier PAC experiments and is caused by the In-related A-centre $^{111}\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ [13]. In contrast, the second defect complex seems to be exclusively correlated with the presence of Ag in CdTe. Performing PAC measurements at different sample temperatures, a similar thermal stability for both defect complexes is observed. Both complexes vanish at a temperature of 500 K and are formed again after slowly cooling the crystal back to ambient temperature.

After heating a CdTe crystal at 800 K and subsequently quenching to 260 K at a cooling rate of about 10^3 K/s, measurements at 77 K showed that the formation of A-centres was strongly suppressed, while the formation of the second defect complex remained almost unaffected (fig. 3b). Taking into account the high diffusion coefficient for Ag in CdTe, it is understandable that the formation of the second complex is still observable after quenching, if it contains a Ag atom. Therefore, this complex is assigned to the $^{111}\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$ pair. That the formation of A-centres could be suppressed by the fast cooling process, indicates the lower mobility of the cation vacancy compared to the Ag impurity. The A-centres are observed to be formed, if following the quench the crystal was warmed up to 295 K (fig. 3c). By measuring the fraction of A-centres as a function of the annealing time at 295 K, a time constant of $\tau = 39(2)$ min for the formation of $^{111}\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pairs is obtained (fig. 4). This time constant agrees fairly well with the time constant of 1 h observed for the formation of $^{111}\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pairs after dipping a CdTe crystal in an aqueous solution of AgNO_3 [14]. Assuming a first order reaction for the formation of $^{111}\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pairs the probability of formation is proportional to the concentrations of In_{Cd} and V_{Cd} , i.e. to $[\text{In}_{\text{Cd}}] \times [\text{V}_{\text{Cd}}]$, yielding the time constant

$$\tau = \frac{e^{E_m/kT}}{\nu_0 \cdot \Omega \cdot ([\text{In}_{\text{Cd}}] + [\text{V}_{\text{Cd}}])}$$

This time constant essentially depends on the migration energy E_m of the cation vacancy and in addition on the concentrations of In donors and cation vacancies, the trapping volume Ω , and the attempt frequency ν_0 . It can be assumed that the concentration $[\text{V}_{\text{Cd}}]$ did not exceed the concentration of Ag atoms of $5 \times 10^{17} \text{ cm}^{-3}$, obtained after diffusion of Ag. Using an attempt frequency of $\nu_0 = 10^{12} \text{ s}^{-1}$ and a trapping volume of

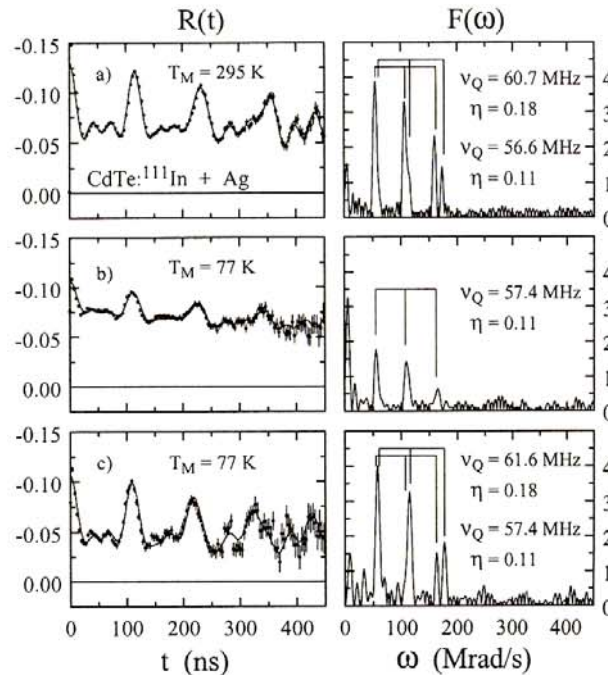


Fig. 3: PAC spectra measured with the probe ^{111}In in CdTe doped with Ag: (a) After diffusion of Ag, (b) after quenching from 800 K to 260 K, and (c) after subsequent warming up to 295 K for 120 min.

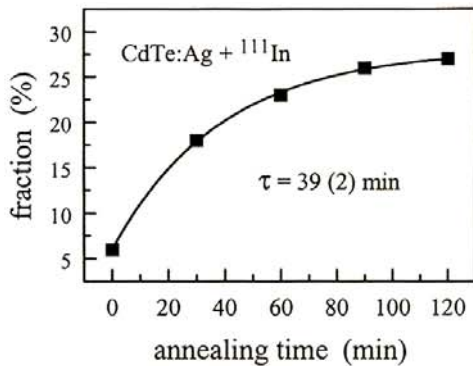


Fig. 4: The fraction of ^{111}In probes, incorporated in the A-centre $^{111}\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ after quenching, as a function of the annealing time at 295 K.

the ^{111}Ag and the ^{111}In probe atom, which also proves the incorporation of Ag as substitutional acceptor.

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$\Omega = 6 \times 10^{-19} \text{ cm}^3$, which agrees with the probability distribution of the s-electron of a hydrogen-like donor, the migration energy of the cation vacancy is estimated to $0.75 \text{ eV} < E_m < 0.85 \text{ eV}$.

SUMMARY

The incorporation of Ag atoms as substitutional acceptors in CdTe is observed in PL and PAC experiments using the radioactive isotope ^{111}Ag . The PAC investigations yield no indication for the formation of close $\text{Ag}_{\text{Cd}}\text{-Ag}_i$ pairs. After thermal treatment of CdTe under Cd pressure, the compensation of Ag_{Cd} acceptors by the formation of $\text{Ag}_{\text{Cd}}\text{-V}_{\text{Te}}$ pairs is observed. The formation of the donor-acceptor pair $\text{Ag}_{\text{Cd}}\text{-In}_{\text{Cd}}$ is detected by both,