# Identification of Ag-acceptor related photoluminescence in [111]Ag doped CdTe

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Bridgman-grown, nominally undoped CdTe crystals were doped with Ag by implanting radioactive [111]Ag. Photoluminescence spectra of the crystals show a donor-acceptor pair (DAP) line at 1.491 eV. The decrease of the intensity of this line with a half life of $T_{1/2} = (7.2 \pm 0.4)$ $d$ is in good agreement with the half life of the $\beta^-$ decay of [111]Ag to [111]Cd of 7.45 $d$. This decrease is not caused by the aging behavior of Ag which was reported in the literature. The data show that the involved acceptor defect contains exactly one Ag atom and confirm the earlier assignment of the acceptor to the $Ag_{Cd}$ defect. Based on the DAP line at 1.491 eV, the spectra did not reveal a contamination of the CdTe crystals by stable Ag. © *1998 American Institute of Physics.* [S0003-6951(98)03723-1]

The group I element Ag is a potential acceptor in CdTe if it is incorporated on a Cd-lattice site ($Ag_{Cd}$). Molva *et al.* reported on photoluminescence (PL) investigations regarding an acceptor level at 108 meV in CdTe.[1] In the PL spectra, the principal bound exciton line at 1.5885 eV, a two-hole transition at 1.5010 eV, and the donor-acceptor pair (DAP) band at 1.491 eV were observed. They also showed the intensities of these PL transitions to be enhanced by diffusing Ag into their crystals. From these experiments the observed acceptor level was assigned to substitutional Ag on a Cd-lattice site.[2] This assignment is not conclusive, though, because the diffusion process used for doping might also produce intrinsic defects as well as defect complexes containing impurities already present in the crystals. Hole concentrations achieved upon doping with Ag do not exceed $2 \times 10^{16}$ cm$^{-3}$. Additionally, a slow decrease of the hole concentration and of the intensities of the $Ag_{Cd}$-related PL lines with a characteristic time of about 15 days while storing Ag-doped crystals at room temperature has been reported.[3] The exact mechanism responsible for this aging behavior has not yet been determined. A complex consisting of substitutional and interstitial Ag ($Ag_{Cd}$-$Ag_i$) has been proposed.[3,4]

In order to verify the identification of the acceptor causing the level at 108 meV with substitutional Ag on a Cd-lattice site, Bridgman-grown, nominally undoped CdTe crystals were implanted with [111]Ag ions at the ISOLDE mass-separator facility at CERN (Geneva). This isotope transmutates into stable [111]Cd via a $\beta^-$ decay with a half life of 7.45 $d$. As a consequence, the concentration of Ag in the crystals decreases with time, and the change of the intensity of a PL line that would be caused by a defect containing a Ag atom can be correlated with the half life of [111]Ag. The implantation was performed with an energy of 60 keV and a maximum dose of $5 \times 10^{13}$ cm$^{-2}$. The CdTe crystals were

prepared before the implantation as follows: They were etched in a solution of 3% bromine in methanol for 30 s, followed by rinsing in methanol to remove traces of bromine. In order to remove the Te film left after etching, the samples were treated in a solution of 1 N KOH in methanol for 6 min. Subsequently, the samples were rinsed in methanol using an ultrasonic bath, in bidestilled water, and in acetone. Finally, the crystals were heated to 500 °C in vacuum for 60 min. After implantation the crystals were annealed at 350 °C for 30 min in vacuum in order to remove implantation-induced radiation damage.

The PL experiments were carried out at 1.8 K, using the 632.8 nm line of a HeNe laser. The beam was attenuated to an intensity of 1 $\mu$W and focused to a diameter of about 150 $\mu$m. The luminescence was analyzed by a 0.5 m grating monochromator and detected by a CCD camera. The position on the sample containing the highest concentration of [111]Ag was determined by monitoring the intensity of the $DAP_{Ag}$ line at 1.491 eV reported by Chamonal *et al.*[2] Although this position was reproduced in all of the measurements with a deviation of less than 100 $\mu$m, the inhomogeneous distribution of defects in the sample resulted in small variations of the intensities of the observed PL signals.

During 47 days, PL spectra were recorded at the sample position with the maximum intensity of the $DAP_{Ag}$ line. Between these measurements the sample temperature never exceeded 150 K in order to avoid modifications of the crystal which were not correlated with the radioactive decay and, in particular, to suppress the aging process, which at room temperature was reported to decrease the intensities of the Ag-related PL lines.[3] In Fig. 1 spectra are shown, which were recorded (a) directly after implantation and annealing and (b) 47 days later, i.e., after [111]Ag had decayed almost completely into [111]Cd. Both spectra show signals from excitons bound to
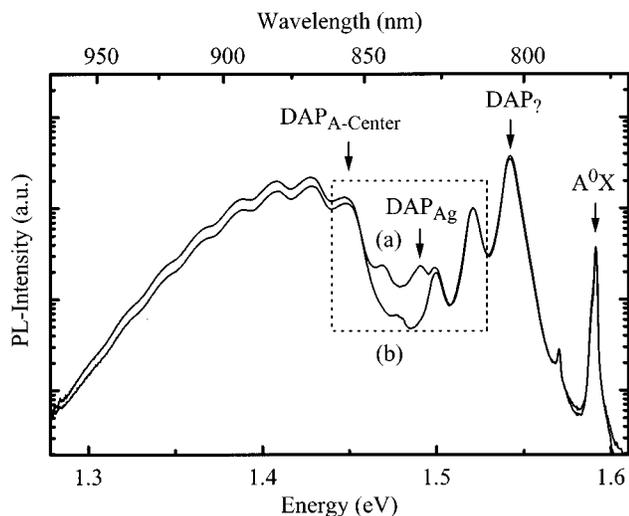
FIG. 1. PL spectra of a CdTe crystal implanted with [111]Ag, which were recorded (a) after implantation and annealing and (b) 47 days later. A blow-up of the dashed region is shown in Fig. 2.



FIG. 3. Intensity of the background-corrected $DAP_{Ag}$ band of Fig. 2 plotted as a function of time.

neutral acceptors ($A^0X$) and several lines originating from donor-acceptor recombinations (DAP). The $DAP_?$ band was also reported by Ossau *et al.*[5] The position and the phonon coupling constant of the $DAP_{A\text{-Center}}$ line is consistent with the assignment to the $(Br-V_{Cd})$ defect.[6] All lines exhibit several phonon replica on the low energy side. In contrast to all other observed lines, the $DAP_{Ag}$-line is only visible in spectrum (a).

In Fig. 2, the blow-up of the PL spectra recorded at various times is shown. The intensities of all spectra are normalized to the intensity of the ($DAP_?$-LO) line, which

best reflects the background around the $DAP_{Ag}$ line. The background is mainly caused by the second and third phonon replica of the $DAP_?$ line besides, possibly, additional unresolved lines. Obviously, the intensity of the $DAP_{Ag}$ line monotonously decreases with time. Quantitatively, the intensities of the $DAP_{Ag}$ line were determined by integrating the PL intensity between 1.481 and 1.495 eV. The background was calculated by applying an exponential fit to these data and was subsequently subtracted. These corrected intensities of the $DAP_{Ag}$ line are plotted logarithmically as a function of time in Fig. 3. The error bars result from the intensity fluctuations of the background, as determined from the minimum between the ($DAP_?$-LO) line and the ($DAP_?$-2LO) line. The exponential fit yields a half life of $T_{1/2}=(7.2\pm0.4)d$, which is in good agreement with the half life of [111]Ag of $T_{1/2}=7.45\ d$. Normalizing the data to a different DAP line of the PL spectrum yields the same half life, but with a larger scatter of the extracted intensities.

The results shown in Figs. 2 and 3 unambiguously confirm the assignment of the DAP line at 1.491 eV to a defect containing [111]Ag because of its decrease with just the half life of the $\beta^-$ decay of the isotope [111]Ag. The observed decrease of the intensity of this line cannot be caused by aging effects because (i) the characteristic time of the aging effect of 15 days is longer even at room temperature and (ii) another heat treatment of the crystal at 350 °C for 30 min in vacuum after recording the last spectrum did not restore the $DAP_{Ag}$ line; Chamonal *et al.* reported that the $Ag_{Cd}$ related lines, which had disappeared due to aging effects, recovered after another heat treatment.[3]

High resolution PL spectra show a change of the intensity of an excitonic line at 1.589 eV that parallels the change of the intensity of the $DAP_{Ag}$ line. This line is probably identical to the line at 1.5885 eV which was assigned to the exciton bound to the $Ag_{Cd}$ acceptor by Chamonal *et al.*[2] A more detailed discussion will be published in Ref. 7. In the energy region above the detection limit of the CCD camera of 1.2 eV, only the $DAP_{Ag}$ line and the excitonic line at 1.589 eV changed their intensities as a function of time. Therefore, it was not possible to verify the assignment of the excitonic line at 1.5815 eV to the $(Ag_{Cd}-Ag_i)$ defect.[3]
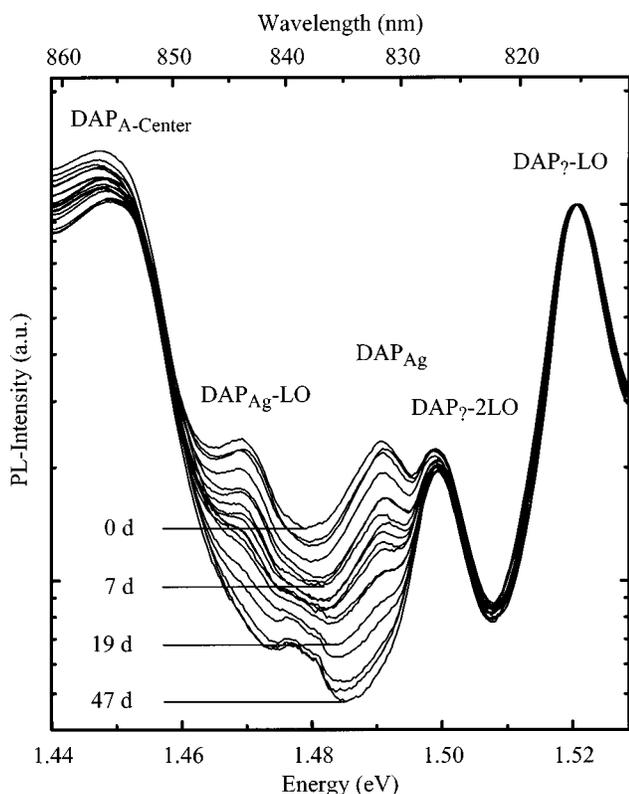


FIG. 2. PL spectra of a CdTe crystal doped with [111]Ag, which were recorded at various times during the 47 days following the [111]Ag implantation.
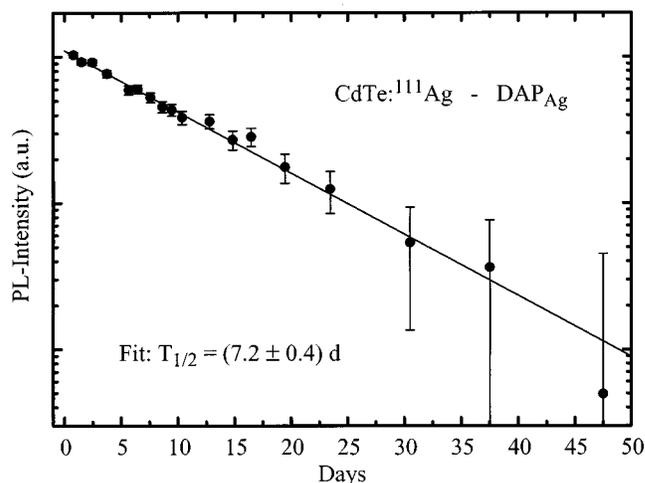
The intensity of the $\beta^-$ particles originating from the decay of $^{111}$Ag was measured at both sides of the sample. Before the heat treatment, $\beta^-$ particles were only detected at the front side. After the heat treatment at 350 °C, the same intensities of $\beta^-$ particles were measured at both sides of the sample. The observed $\beta^-$ intensities indicate a homogeneous distribution of the $^{111}$Ag atoms across the entire thickness of the CdTe crystal of about 0.5 mm. A high Ag concentration only near the surfaces of both sides of the crystal as a result of transport via the gas phase is excluded, because $^{111}$Ag atoms would be expected to cover also part of the quartz ampoule used for the annealing procedure, which was not observed. The PL spectra, on the other hand, showed the DAP$_{Ag}$ band only within the implanted area of the sample. Both observations can be explained if two diffusion mechanisms for Ag in CdTe are assumed, as was discussed for HgCdTe.[8] Most of the $^{111}$Ag atoms diffuse via a fast mechanism, which leads to an almost homogeneous distribution across the 0.5-mm-thick sample already after diffusion at 350 °C for 30 min and causes the same $\beta^-$ intensities if measured from the front or the back side of the sample. The concentration of these $^{111}$Ag atoms, however, is below the detection limit of the DAP$_{Ag}$ line. The smaller fraction of $^{111}$Ag atoms diffuse via the slow mechanism. They are still concentrated near the implanted region of the sample, thereby causing the DAP$_{Ag}$ line observed by PL.

Magerle *et al.* showed that the PL intensity originating from a particular defect is not necessarily proportional to its concentration within the crystal.[9] This holds especially if only part of the volume probed by PL contains this defect and if, at the same time, its concentration is high enough to present a major channel for charge carrier recombination. At least the second condition is not fulfilled in the present ex-periment because of the broad depth distribution of the Ag atoms following the heat treatment after implantation, as was indicated by the $\beta^-$ intensities. A very low concentration of $^{111}$Ag atoms in the volume analyzed by PL is also concluded from the saturation of the DAP$_{Ag}$ line, which occurs at an excitation power of less than 1 $\mu$W. Hence, the agreement of the half life of the DAP$_{Ag}$ line with the half life of $^{111}$Ag shows, besides the relationship of the DAP$_{Ag}$ line to the presence of Ag, that the acceptor causing the level at 108 meV contains exactly one Ag atom and confirms the identification of the acceptor as the Ag$_{Cd}$ defect. Finally, it should be noted that the complete disappearance of the DAP$_{Ag}$ line shows that the CdTe crystals used in these experiments did not contain detectable traces of stable Ag.

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