Identification of Ag-acceptors in ^{111}Ag/^{111}Cd doped ZnTe and CdTe

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Abstract

Nominally undoped ZnTe and CdTe crystals were implanted with radioactive ^{111}Ag, which decays to ^{111}Cd, and investigated by photoluminescence spectroscopy (PL). In ZnTe, the PL lines caused by an acceptor level at 121 meV are observed: the principal bound exciton (PBE) line, the donor-acceptor pair (DAP) band, and the two-hole transition lines. In CdTe, the PBE line and the DAP band that correspond to an acceptor level at 108 meV appear. Since the intensities of all these PL lines decrease in good agreement with the half-life of ^{111}Ag of 178.8 h, both acceptor levels are concluded to be associated with defects containing a single Ag atom. Therefore, the earlier assignments to substitutional Ag on Zn- and Cd-lattice sites in the respective II-VI semiconductors are confirmed. The assignments in the literature of the S_1, S_2, and S_3 lines in ZnTe and the X_1^{Ag}, X_2^{Ag}/C_1^{Ag}, and C_2^{Ag} lines in CdTe to Ag-related defect complexes are not confirmed.

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1. Introduction

Photoluminescence (PL) spectra reveal a lot of defect levels in semiconductors, but it is often difficult to identify the chemical nature of the impurity causing a particular defect level. An unambiguous chemical identification can be achieved if radioactive isotopes are used as dopants. Depending on whether the parent or the daughter isotope is the dopant element, the dopant concentration decreases or increases with the characteristic half-life of the radioactive decay, respectively. If the intensity of a PL line is correlated with the half-life of the radioactive decay, the parent or daughter isotope can be identified as a constituent of the defect causing the observed level [1].

The element Ag is an unintentional impurity in both ZnTe and CdTe, which is important for understanding the electrical and optical properties of these materials [2]. In the PL spectra of undoped ZnTe, lines corresponding to an acceptor level at 121 meV are observed: the principal bound exciton line (PBE) at 2.3740 eV (A_1^{Ag}), which is caused by the recombination of excitons bound to this acceptor, and the corresponding two hole transitions (THT) [3, 4, 5]. The THT, excitonic recombinations that leave the remaining hole in an excited state, are observed at 2.2737 eV (A_2^{Ag}), 2.2630 eV (A_3^{Ag}), and in the energy range between 2.2587 eV and 2.2530 eV ($A_{n\geq4}^{Ag}$). Magnea et al. show the intensities of these PL transitions to be enhanced by diffusion of Ag into ZnTe crystals and assign the observed acceptor level to substitutional Ag on a Zn-lattice site (Ag_{Zn}) [4]. The same series of PL lines, however, appear after annealing the crystal at 750 °C for 7 days in a Zn or Te atmosphere [3]. Additionally, the bound exciton lines S_1 at 2.3149 eV, S_2 at 2.3486 eV, and S_3 at 2.365 eV are created by diffusion of a high concentration of Ag into ZnTe. S_1 is assigned to pairs of substitutional and interstitial Ag. S_2 and S_3 are tentatively identified with defects which are composed of three atoms involving Ag [6, 7].

In CdTe, the situation is very similar: Molva et al. report on PL investigations regarding an acceptor level at 108 meV in undoped CdTe. The A_1^{Ag} line at 1.5885 eV, the A_2^{Ag} line at 1.5010 eV, and the donor-acceptor pair (DAP_{Ag}) band at 1.491 eV are observed [8]. Again, the intensities of these PL lines are shown to be enhanced by diffusion of Ag into CdTe, and

the observed acceptor level is assigned to Ag_{Cd} defects [9]. Using radioactive ^{111}Ag, this assignment is confirmed for the DAP_{Ag} band, but not for the excitonic lines A_1^{Ag} and A_2^{Ag} [10]. Storing Ag-doped CdTe crystals at room temperature for several weeks creates the lines X_1^{Ag} at 1.5880 eV [11], X_2^{Ag} at 1.5815 eV [11], also called C_1^{Ag} [12], and C_2^{Ag} at 1.5583 eV [12]. The C_1^{Ag} line is tentatively attributed to pairs of substitutional and interstitial Ag or to complexes of Cd vacancies and interstitial Ag [11].

All these assignments in both ZnTe and CdTe are not conclusive, though, because the diffusion process used for doping also produces intrinsic defects and possibly defect complexes containing impurities already present in the crystals. In order to verify the above assignments, ZnTe and CdTe were doped with ^{111}Ag, which decays to ^{111}Cd with a half-life of $t_{1/2} = 178.8$ h [13], and investigated by PL.

2. Experimental procedure

Bridgman-grown, nominally undoped ZnTe and CdTe crystals of typically $3 \times 3 \times 0.5$ mm^3 were implanted with ^{111}Ag ions at the ISOLDE mass-separator facility (CERN, Geneva). The implantation was performed with a dose of $5 \cdot 10^{13}$ cm^{-2} and an energy of 60 keV, resulting in an average implantation depth of 30 nm. In order to remove implantation-induced damage, the ZnTe crystals were annealed at 700 K for 30 min in a Te atmosphere and the CdTe crystals were annealed at 620 K in vacuum. Since Ag is a fast diffuser in both ZnTe and CdTe [3, 14], the diffusion occurring during this annealing process resulted in a broad depth distribution and, as a consequence, in a low concentration of the ^{111}Ag atoms.

The PL measurements were carried out at 1.8 K. The 351.1 nm line of an Ar laser, which was attenuated to 10 mW and focussed to a diameter of about 200 µm, was used for excitation. The luminescence was analysed by a 0.5 m grating monochromator and detected by a CCD camera.

3. Experimental results and discussion

In order to look for the changes of the PL spectra due to the element transmutation, PL measurements were performed at various times after annealing. Between these measurements the temperature never exceeded 150 K and, therefore, modifications of the crystals, which were not induced by the radioactive decay, probably did not occur.
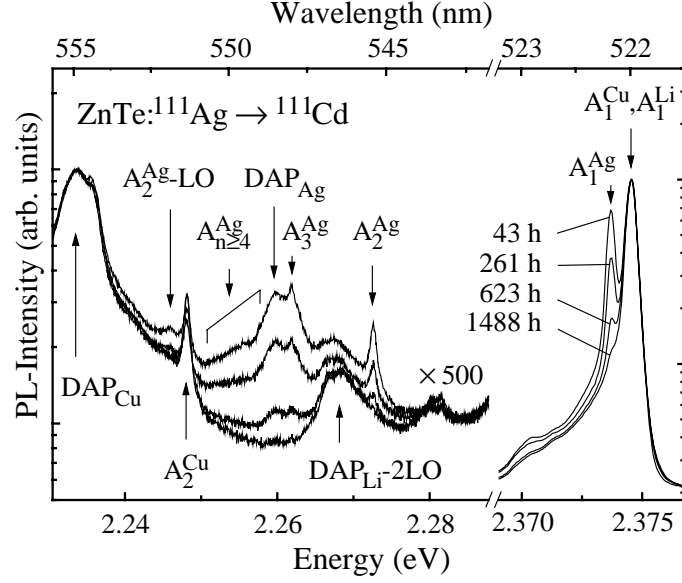
Fig. 1. *PL spectra of a ZnTe crystal implanted with ^{111}Ag, which were recorded at different times after annealing (700 K, Te atmosphere, 30 min).*

a) ZnTe

A subset of the PL spectra obtained from ZnTe is shown in Fig. 1. It consists of two parts, the PBE region near the band edge and the THT region at lower energies. In each part, the intensities of the spectra are normalised to the intensity of the dominating PL line, i.e. the intensities in the PBE region are normalised to the intensity of the unresolvable A_1^{Cu} and A_1^{Li} lines at 2.3746 eV [4, 5] and the intensities in the THT region are normalised to the DAP_{Cu} band at 2.234 eV [4]. Cu and Li are usually present as unintentional impurities in both ZnTe and CdTe. The intensities of all lines that correspond to the acceptor level at 121 meV monotonously decrease with time, whereas the intensities of the Cu- and Li-related lines remain constant. The seeming decrease of the intensities of the DAP_{Li}-2LO band and the A_2^{Cu} line is due to the decreasing intensities of the neighbouring Ag-related lines. If compared with Ref. [4], the PL spectra show that the lines $A_{n \geq 4}^{Ag}$ are not resolved into single lines and the DAP_{Ag} band at 2.260 eV is clearly visible. The observation of the DAP_{Ag} band in this experiment is probably due to a higher donor concentration in our crystals. The S_1, S_2, and S_3 lines are not observed (see below).

Figure 2 shows the intensities of a) the A_1^{Ag} line, b) the A_2^{Ag} line, and c) the sum of the $A_{n \geq 3}^{Ag}$ lines and the DAP_{Ag} band, logarithmically plotted as a function of time. The intensities are determined by integrating the intensities in the energy ranges between 2.3735 eV and

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2.3740 eV, between 2.2718 eV and 2.2739 eV, and between 2.2516 eV and 2.2643 eV, respectively. The exponential fits yield half-lives $t_{1/2} = 170\pm10$ h, $t_{1/2} = 188\pm30$ h, and $t_{1/2} = 213\pm30$ h, which are in good agreement with the half-life $t_{1/2} = 178.8$ h of ^{111}Ag.
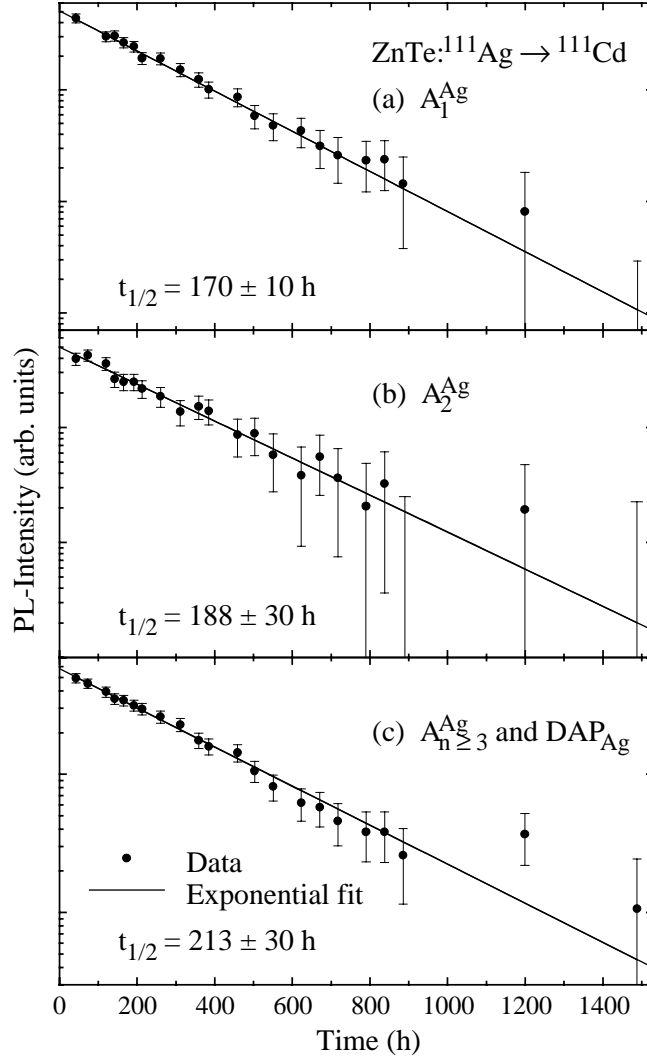
Fig. 2. *Intensity of (a) the A_1^{Ag} line, (b) the A_2^{Ag} line, and (c) the sum of the $A_{n\geq3}^{Ag}$ lines and the DAP_{Ag} band in ZnTe, logarithmically plotted as a function of time after annealing. The constant background, determined from the exponential fit, is already subtracted from the experimental data.*

Normalising the data to other lines in the PL spectrum yields similar results, but with a larger scatter of the extracted intensities. In accordance with the literature [3, 14], the diffusion occurring during the annealing process resulted in a low concentration of ^{111}Ag, which is concluded from the low intensities of the Ag-related lines. They are not stronger than the lines related to the Li and Cu impurities, which are usually present in the order of 10^{15} cm^{-3}.

Therefore, the indirect effects discussed in Ref. [15] and in Ref. [1], which are connected with the change of the doping concentration through the radioactive decay and affect the observed intensities as well, are not relevant, because these effects are only important at high doping levels of radioactive isotopes. Hence, the observed insensitivity to the normalisation is due to the low concentration of ^{111}Ag.
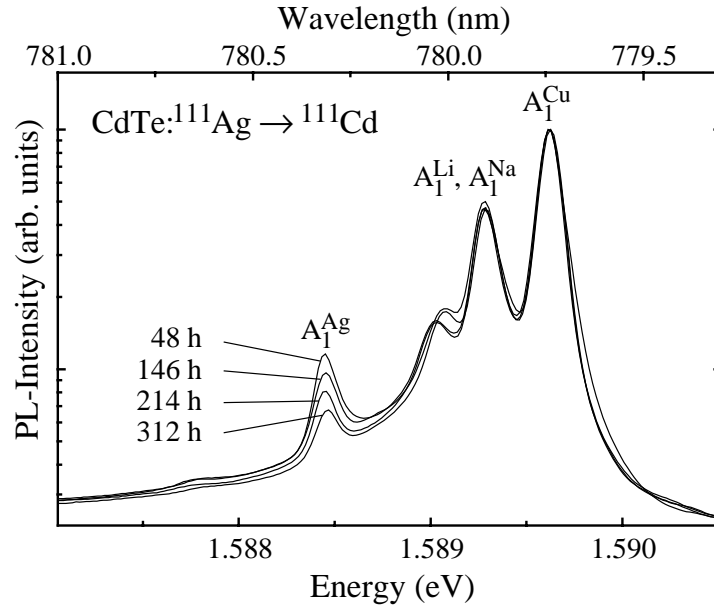

Fig. 3. *PL spectra of a CdTe crystal implanted with ^{111}Ag, which were recorded at different times after annealing (620 K, vacuum, 30 min).*

b) CdTe

In Fig. 3 a subset of the PL spectra obtained from CdTe is shown. The intensities are normalised to the intensity of the A_1^{Cu} line at 1.5896 eV [9]. Obviously, the intensity of the A_1^{Ag} line at 1.5885 eV decreases with time. Its intensity is determined by integration of the intensities between 1.5883 eV and 1.5887 eV and logarithmically plotted in Fig. 4. The best fit is obtained with $t_{1/2} = 150 \pm 40$ h, which agrees well with the half-life of ^{111}Ag. For the DAP_{Ag} band at 1.491 eV, the agreement with the half-life of ^{111}Ag has been shown previously [10]. The A_2^{Ag} line is not observable because it is covered by the $DAP_{Li, Na}$ transitions (not shown). The X_1^{Ag}, X_2^{Ag}/C_1^{Ag}, and C_2^{Ag} lines are not observed, either (see below).

For both ZnTe and CdTe, the presented results unambiguously confirm that the acceptor levels at 121 meV and 108 meV are associated with defects containing a single Ag atom.
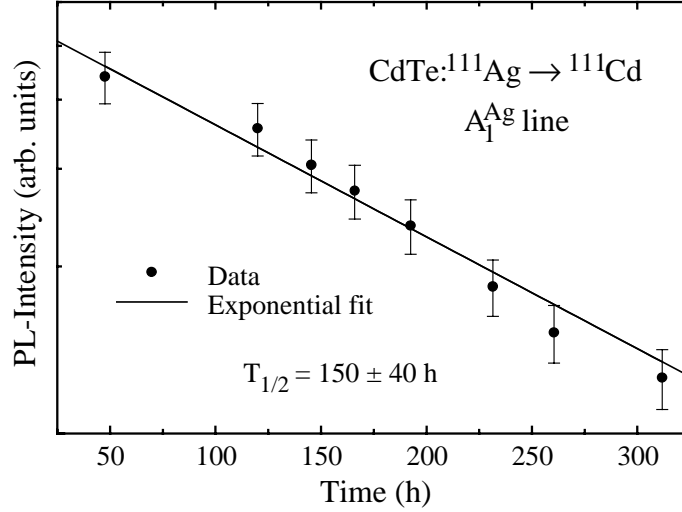
Fig. 4. *Intensity of the* A_1^{Ag} *line in CdTe, logarithmically plotted as a function of time after annealing. The background, determined for each spectrum individually, is already subtracted from the experimental data.*

Taking into account the T_d symmetry of these acceptors, which was previously shown [5, 16], the present data verify the assignments to the Ag_{Zn} and Ag_{Cd} defects in ZnTe and CdTe, respectively. In addition to the lines caused by these acceptor levels, no lines are observed that change their intensities during the decay of ^{111}Ag. In particular, the S_1, S_2, and S_3 lines in ZnTe and the X_1^{Ag}, X_2^{Ag}/C_1^{Ag}, and C_2^{Ag} lines in CdTe are not observed. Since the absence of these lines might be due to the low Ag concentrations in the crystals, both Bridgman-grown bulk crystals and MOCVD-grown films of the two materials ZnTe and CdTe were implanted with a higher dose of $5 \cdot 10^{14}$ cm^{-2} stable Ag ions and annealed in various atmospheres at various temperatures. Although the Ag concentration in these crystals is higher, especially in the MOCVD-grown films being only 1 μm thick, the lines looked for are not observed, either, not even after storing the crystals and films at room temperature for several weeks. Therefore, the assignments of the S_1, S_2, and S_3 lines in ZnTe and the X_1^{Ag}, X_2^{Ag}/C_1^{Ag}, and C_2^{Ag} lines in CdTe to Ag-related defects are not confirmed.

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