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MOCVD grown CdTe investigated by photoluminescence and PAC

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Abstract

Comparative investigations, using perturbed $\gamma\gamma$-angular correlation and photoluminescence spectroscopy, were performed on CdTe films grown on GaAs substrates by MOCVD. The incorporation of the radioactive probe atoms ^{111}In into the CdTe films was done via diffusion, implantation, and, for the first time, by in situ doping during MOCVD growth. The latter process was realised by using a modified MOCVD reactor with the precursor trimethylindium (TMIn) labelled with the radioactive isotope ^{111}In. The influence of the doping procedure and the thermal treatment, including annealing under Cd or Te overpressure, was investigated. For two donor–acceptor pairs, involving the donor In and the acceptors As or the Cd vacancy, the results of both techniques were correlated.

1. Introduction

The investigation of defects in II–VI semiconductors, especially the effect of self compensation, has received a lot of interest in the last few years. A large amount of information published about properties and behaviour of intrinsic and extrinsic defects in these materials is based on investigations, which use photoluminescence spectroscopy (PL) [1], often in combination with electrical characterisation techniques, such as I–V/C–V, DLTS or Hall measurements [2]. Since these methods, being highly sensitive to the presence of defects, give little information about the chemical and structural properties of defects, methods like EPR [3,4] and perturbed $\gamma\gamma$-angular correlation (PAC) [5] are needed, both of which are sensitive to the hyperfine interaction of a localised probe with its immediate lattice surrounding.

CdTe films, grown on GaAs by MOCVD, were investigated by combining the integral information, supplied by PL, with the microscopic sensitivity of the PAC method. The investigated defects include intrinsic defects, which are created either during growth or during post growth treatment, including annealing under Cd and Te, as well as extrinsic defects. The extrinsic defects are added either intentionally by in situ doping or ex situ diffusion, or unintentionally via contamination arising from the growth process or out-diffusion from the substrate. As reference for the quality of the investigated CdTe layers, bulk crystals, doped via implantation, were used for the PAC and PL measurements.

2. Experimental procedure

CdTe films were grown on GaAs by MOCVD, using the precursors di-isopropyltellurium (DIPTe) and dimethylcadmium (DMCd). The (100) GaAs

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substrates were etched in a 5 : 1 :1 solution of H_2SO_4, H_2O and H_2O_2 and heated at 893 K. For the growth process the Te to Cd ratio was varied between 1 : 1 and 3 : 1 and the substrate temperature between 633 and 693 K. The thickness of the films was about 1 μm, determined by SIMS measurements. Doping with the donor In was performed using the precursor trimethylindium (TMIn).

Thereby, doping with the radioactive isotope ^{111}In, the most commonly used probe atom for PAC has, for the first time, been achieved in situ, during the MOCVD process. A mixture of radioactive TM^{111}In and stable TMIn was produced in a process described by Clark et al. [6] for stable TMIn, whereby the set-up was adapted to the requirements of working with extremely small amounts of radioactive material. The mixture, containing the radioactive precursor, was introduced into a commercially available MOCVD system via a specially constructed phial. The efficiency of the doping process was controlled in a quantitative way by measuring the distribution of the radioactive isotope ^{111}In within the MOCVD system. The isotope ^{111}In was introduced also by diffusion and implantation.

The samples were characterised directly after growth and following each annealing step. The heat treatment was performed under vacuum or in the presence of Cd, Te or additional dopant atoms, like In, with the samples sealed within an evacuated quartz ampoule.

PAC measurements were performed at the probe ^{111}In in order to detect the hyperfine interaction between the electric field gradient (EFG), which arises from the immediate lattice surrounding at the site of the probe atom, and the quadrupole moment of the isotope ^{111}Cd, which is populated via the radioactive decay of the probe ^{111}In. A non-zero EFG, which is the result of a deviation of the electronic charge distribution about the probe from spherical symmetry, is observed in case of a non-cubic lattice structure or a point defect within one or two atomic distances of the probe atom. The EFG is the second spatial derivative of the electrostatic potential and, therefore, can be described by a second rank, traceless tensor. In its principal axis system this tensor is completely described by two quantities, usually its largest component V_{zz}, expressed via the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. By detecting two γ-quanta in coincidence, which are emitted following the radioactive decay of ^{111}In, a time spectrum described by:

$$R(t) = s_0 + \sum_{n=1}^{3} s_n \cos(\omega_n t), \tag{1}$$

is obtained, which holds for the case of a single EFG. The frequencies ω_n are extracted from the Fourier transform $F(\omega)$, yielding $\nu_Q \sim \omega_1$ and η, which is determined by the ratio ω_2/ω_1. A more detailed description of the PAC technique can be found in Ref. [7]. All PAC spectra were recorded at 295 K.

PL measurements were performed at 1.6 K, using the 632.8 nm line of a HeNe laser with an output power of 15 mW. The spectra were recorded with a scanning spectrometer, having a focal length of 500 mm and a maximum resolution of 0.1 nm.

3. Experimental results

3.1. PAC experiments

To show the influence of the doping process on the incorporation of the In atoms into the MOCVD grown CdTe layers, the PAC spectra obtained after different doping procedures are compared in Fig. 1a and Fig. 1b. The PAC data in Fig. 1a were measured directly after growth whereby the sample was homogeneously doped in situ with a mixture of stable In and radioactive ^{111}In. In Fig. 1b the result of the ex situ diffusion of radioactive ^{111}In into an epilayer, grown under similar conditions is shown; the diffusion temperature used of 700 K was close to the growth temperature of 658 K. Both spectra are dominated by two EFG, characterised by quadrupole coupling constants $\nu_Q = 103$ MHz and $\nu_Q = 113$ MHz and asymmetry parameters $\eta = 0.12$ and $\eta = 0.2$, respectively. The only observable difference is the higher level of incorporation of probes on cubic lattice sites for the in situ doped sample (Fig. 1a), which is evident from the slightly larger time independent offset in the spectrum. The ex situ doped sample was subsequently exposed to Te (Fig. 1c) and to Cd vapour (Fig. 1d) at 700 K. After diffusion with

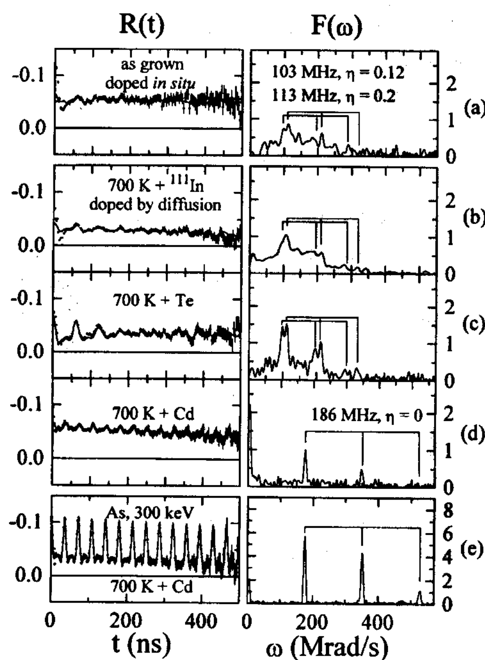

Fig. 1. PAC spectra: (a–d) In doped CdTe films grown by MOCVD on GaAs; (e) CdTe bulk crystal, implanted with As (300 keV), annealed at 700 K under Cd vapour.

Te, the fraction of ^{111}In atoms exposed to these two EFG is increased, while annealing under Cd vapour leads to a total disappearance of these EFG and, at the same time, to the occurrence of a new EFG, characterised by $\nu_Q = 186$ MHz, $\eta = 0$. This EFG is also observed in CdTe bulk crystals that were implanted with As and ^{111}In and annealed at 700 K (Fig. 1e). In addition, the fraction of probe atoms in Fig. 1d located on unperturbed lattice sites is increased.

3.2. Photoluminescence and electrical measurements

PL spectra, measured on in situ In doped CdTe films ([In] ≈ 10^{18} cm^{-3}), are shown in Figs. 2a–2f. The samples were grown and treated under conditions that were comparable to those used for the PAC experiments. A sharp GaAs substrate peak is visible in all spectra at 1.49 eV [8]. It is used for normalisation of the intensities in order to compare the relative changes of intensities induced by the thermal treatment.

The spectrum measured directly after growth (Fig. 2a) is dominated by a broad DAP band, centred around 1.44 eV, and very weak excitonic features are visible around 1.59 eV. Electrical measurements show that the In donors, introduced during growth, are almost fully compensated. Annealing at 700 K for 30 min under Te vapour leads to an enhancement of the observed DAP band with a slight shift to lower energies (Fig. 2b) and leaves no detectable signal in the excitonic region of the spectrum. Heat treatment under Cd vapour, beginning at 600 K (Fig. 2c), effects a decrease of the observed DAP band and, at the same time, increases the intensity of the bound exciton emission. After annealing at 700 K under Cd vapour (Fig. 2d), the DAP band disappears completely, while the spectrum now is dominated by donor bound excitons. Electrical measurements show that nearly 100% of the In atoms are electrically active. In addition, first signs of a new DAP signal with a zero phonon line at 1.51 eV become visible. Further annealing under Cd at 800 K again decreases the carrier concentration and, at the same time, in-

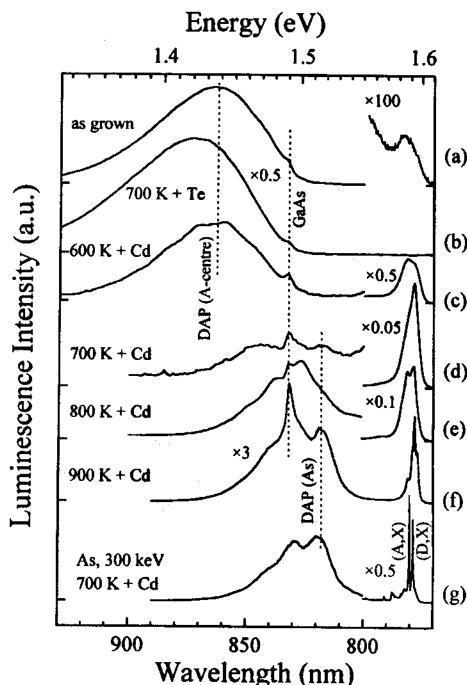

Fig. 2. PL spectra: (a–f) In doped CdTe films grown by MOCVD on GaAs, intensity normalised using the GaAs substrate peak at 1.49 eV; (g) CdTe bulk crystal implanted with As at 300 keV, annealed at 700 K under Cd vapour.

creases the intensity of the new DAP signal significantly (Fig. 2e). Excitonic emission, acceptor bound as well as donor bound, is observed with high intensity. Heating under Cd at 900 K (Fig. 2f) results in a strong decrease in the overall signal strength, possibly due to an evaporation of CdTe, and the half width of the observed excitonic lines decreases. The DAP at 1.51 eV is still clearly visible. The same DAP band is observed in a reference CdTe bulk crystal after implantation with As and annealing under Cd vapour at 700 K (Fig. 2g).

4. Discussion

Two different donor–acceptor pairs in CdTe have been observed in the PAC as well as in the PL measurements, presented here. One of them is probably caused by the presence of Cd vacancies and the other one by As atoms.

The occurrence of the two EFG, characterised by $\nu_Q = 103$ MHz, $\eta = 0.12$ and $\nu_Q = 113$ MHz, $\eta = 0.2$, is directly correlated to the broad defect band located around 1.44 eV. This PL signal has been assigned to the so called A-centre, which is a donor–acceptor pair, consisting of a Cd vacancy (V_{Cd}) as acceptor and, in this case, of the donor In [9,10]. This assignment is supported by the results obtained after heat treatment under Te and Cd vapour, which shows an enhancement (Figs. 1c and 2b) or a disappearance (Figs. 1d and 2c) of the defect, respectively. The assignment to an In–V_{Cd} pair, however, is not supported by PAC because this pair has already been assigned to a different EFG, characterised by $\nu_Q = 60$ MHz, $\eta = 0.1$ [5,11]. Since the defect under discussion is only observed in highly In doped CdTe, with In concentrations above 10^{17} cm^{-3} [12], rather an assignment to a more complex defect structure, involving probably two In atoms, paired with a Cd vacancy, is proposed. In this case, it has to be assumed that the energetic position of the PL peak is not sensitive to an attachment of a second In atom to the A-centre. The interpretation of the present data, however, has to await further investigations because the two EFG observed here might still be connected with the A-centre but in a different charge state.

The second defect, characterised by the EFG with $\nu_Q = 186$ MHz, $\eta = 0$ [13] and by the DAP line at 1.51 eV, is obviously correlated with the presence of As in the CdTe samples and is assigned to an In–As pair. Fig. 1e shows the identical EFG if CdTe is implanted with As. The PL line at 1.51 eV was also reported for MOCVD grown CdTe, doped with triethylarsine, by Ekawa et al. [14]. Obviously, in Figs. 1d and 2d–2f the diffusion of As from the GaAs substrate into the CdTe layer leads to an electrical passivation of the In atoms in CdTe because As atoms act as acceptors on Te lattice sites.

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