



Doping of CdTe with radioactive ^{111}In during MOCVD growth

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Abstract

CdTe epilayers grown on GaAs by MOCVD were doped in situ with the donor In by using a mixture of radioactive trimethylindium (TM^{111}In) and stable TIn . By measuring the γ -radiation of the radioactive dopant ^{111}In the amount of In atoms incorporated into the CdTe layers during growth and the deposition of In within the MOCVD setup was determined. The presence of compensating defects in the grown layers was detected at the site of the donor ^{111}In by the perturbed $\gamma\gamma$ -angular correlation (PAC) technique. The PAC experiments, complemented by photoluminescence spectroscopy, show the presence of A-centres, consisting of a Cd vacancy and an In donor. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Growth techniques, like MBE and MOCVD, have overcome a part of the problems that involve the self-compensation encountered in the doping of II–VI compounds [1]. In spite of this success, the failure to produce most of these semiconductors with high carrier concentrations of both n-type and p-type is still not fully understood. In this paper, the growth of In-doped CdTe epilayers on GaAs substrates by MOCVD is reported using radioactive trimethylindium (TM^{111}In) as a precursor.

By employing the radioactive tracer ^{111}In as a donor, an analytical approach is introduced that

supplies unique information about the mass transport of the In precursor during the MOCVD process. Additionally, the related dissociation properties of the precursor are accessible and, at the same time, a tool for the characterisation of defects on an atomic scale is offered. In detail, the following information was obtained in the experiments presented here: (i) A quantitative determination of the amount of In atoms incorporated into the CdTe layers during growth. (ii) An assessment of precursor-adsorption in the gas pipework of the MOCVD setup. (iii) The dissociation efficiency of the precursor at different growth temperatures. (iv) The characterisation of point defects in the epilayers by the isotope ^{111}In , which represents a well known probe atom for the perturbed $\gamma\gamma$ -angular correlation technique (PAC). The reproducible and non-destructive introduction of PAC probe atoms into epitaxial

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layers usually presents a major obstacle, which can be overcome by introducing the probe atoms during the growth process.

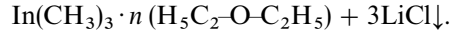
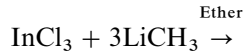
2. Experimental technique

CdTe was grown in a commercial MOCVD system (Thomas Swan Ltd.) at atmospheric pressure, using the precursors dimethylcadmium (DMCd), diisopropyltellurium (DiPTe), and as doping sources TMIIn and radioactive ^{111}In . The CdTe epilayers were grown on GaAs substrates, which were supported by a tilted, heated graphite susceptor. Best results for undoped and In-doped crystals were obtained at growth temperatures in the range between 663 and 673 K with a Te : Cd ratio of 3 : 1.

PAC measurements were performed at the probe ^{111}In in order to detect the hyperfine interaction between the defect-related electric field gradient (EFG) and the quadrupole moment Q of the isomeric level of the probe's daughter isotope ^{111}Cd . Because of the cubic zinc blende lattice of the CdTe crystal, a non zero EFG indicates the presence of a point defect within one or two atomic distances to the probe atom. The EFG is described by two quantities, its largest component V_{zz} , expressed via the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. Detecting the two γ -quanta emitted after the radioactive decay of ^{111}In in coincidence, the PAC time spectrum $R(t)$ is obtained, which yields the three frequencies ω_1 , ω_2 , and $\omega_3 = \omega_1 + \omega_2$ characterising a single EFG. From these frequencies, the parameters ν_Q and η are determined. A more detailed description of the PAC technique and its application to semiconductors can be found in Ref. [2].

For the MOCVD process, the radioactive ^{111}In probes have to be chemically incorporated into a suited precursor. The precursor chosen for this purpose was TMIIn, which is commonly used for donor doping of II–VI materials. For the sake of radioprotection, the number of radioactive ^{111}In atoms is limited to less than 10^{14} . For the chemical reaction, which needs a minimum of about 10 mg of InCl_3 , a mixture of radioactive and stable InCl_3 was used, yielding a ratio of radioactive to stable In

of $1 : 2 \times 10^5$. As described by Clark et al. [3], methyl lithium (LiCH_3) dissolved in ether was used as the source for the alkyl-groups.



The reaction product was evaporated at low pressure and transferred into a cooled phial, which subsequently was connected directly to the MOCVD system. The growth process was monitored by a γ -detector, which recorded the presence of In atoms via the γ -activity of the radioactive tracer ^{111}In .

3. Results and discussion

3.1. Mass transport

The In content as calculated from the γ -activity, measured in situ at the site of the grown CdTe epilayers, is plotted as a function of the growth time in Fig. 1. The incorporation of In during two growth processes, which differ in the composition of the metalorganic In source material, is shown. The first process (closed circles), utilised a TMIIn-ether adduct for doping, while the second process (open squares) used the dried TMIIn that was left by the first growth process. In the first run, which results in the doping of CdTe with 1.2×10^{16} In atoms, during the first 40 min of growth no γ -activity is measured at the site of the substrate, showing that no In is incorporated into the layer during this time. In the second run, the γ -activity starts to rise immediately after the start of the growth process. Two mechanisms might explain the observed delay in the first run: (i) Excess ether bound to the precursor was inhibiting the transport of TMIIn. First, the transport of the ether out of the phial was required, leaving the dried TMIIn behind. (ii) The adsorption of TMIIn in the pipework of the MOCVD system had to saturate, which takes several minutes, before the precursor could reach the reactor.

The influence of the substrate temperature on the incorporation of In into the CdTe layers was

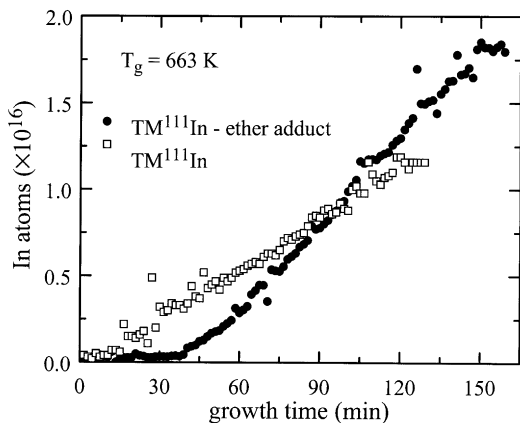


Fig. 1. In atoms incorporated into a CdTe epilayer during the MOCVD process for two different chemical states of the radioactive precursor TM^{111}In .

investigated by variation of the substrate temperature, keeping all other parameters fixed. No significant variation of the In concentration being around 10^{20} cm^{-3} was observed in the temperature range between 633 and 663 K. In contrast, at 703 K the In content strongly increased up to 10^{22} cm^{-3} at otherwise identical conditions. In this case, the In constituted a major component of the grown layer as will be discussed in the context with the PAC measurements in Fig. 3b.

The distribution of In atoms within the MOCVD setup was determined by measuring the γ -activity at several positions. At growth temperatures suited for epitaxy of CdTe around 653 K, less than 1% of the In delivered by the phial was incorporated into the layer. About the same amount was adsorbed on the reactor walls, while the heated graphite susceptor contained more than 10% of the original In supply, even though the uncovered geometric surface of the susceptor was comparable to the size of the substrate. A fraction of about 60% of the supplied In was deposited in the charcoal filter downstream of the reactor. Beyond this filter, in the pipework or in the cracking furnace, no γ -activity was observed.

A small fraction of the TMIn supplied by the phial was adsorbed in the pipework leading to the reactor. As reported in the literature [4], this material can be used for controlled low-level doping

with In by desorption of the TMIn in subsequent growth runs. In the present experiments, the amount of adsorbed In was determined after dismantling parts of the MOCVD pipework by measuring the local γ -activity. The number of In atoms per cm was estimated to about 10^{16} , resulting in 10^{18} adsorbed TMIn molecules over the total length of 1 m of pipework. Since the adsorbed material can still be transported to the reactor in subsequent runs, the adsorbed TMIn is obviously not decomposed.

3.2. Characterisation of defects

For a CdTe layer grown at 663 K with the conditions described above and doped in situ with ^{111}In , Fig. 2 shows the results of PAC experiments. Directly after growth without any additional treatment, about 20% of the probes detected in the sample are incorporated in an unperturbed cubic surrounding, as indicated by the constant offset in the PAC time spectrum $R(t)$ (Fig. 2a). These In atoms are situated on regular Cd lattice sites of the CdTe crystal, which is an important prerequisite for introducing electrically active dopant atoms. A smaller fraction of about 6% is situated at sites close to a point defect, which is characterised by two specific EFG of $\nu_{Q1} = 103 \text{ MHz}$, $\eta_1 = 0.12$ and $\nu_{Q2} = 113 \text{ MHz}$, $\eta_2 = 0.2$ as shown in the Fourier transform $F(\omega)$ of the PAC time spectrum. They are known to occur in highly n-type doped CdTe [5] and are explained in terms of an A-centre consisting of the donor ^{111}In and a Cd vacancy [6,7]. The remaining In atoms are incorporated at lattice sites having no unique surrounding. Annealing the layers for 30 min at 770 K in vacuum increased the fraction of probe atoms close to a Cd vacancy to about 20% while the amount of probe atoms on unperturbed Cd sites remained constant (Fig. 2b). Annealing the layers in Te vapour produced the same results. In contrast, if the layers were annealed for 30 min at 700 K under Cd vapour no $^{111}\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pairs were detected but about 78% of the In atoms were located at Cd sites with only a slight perturbation of the cubic symmetry (Fig. 2c).

The growth of CdTe layers was no longer observable if the growth temperature was raised to 703 K.

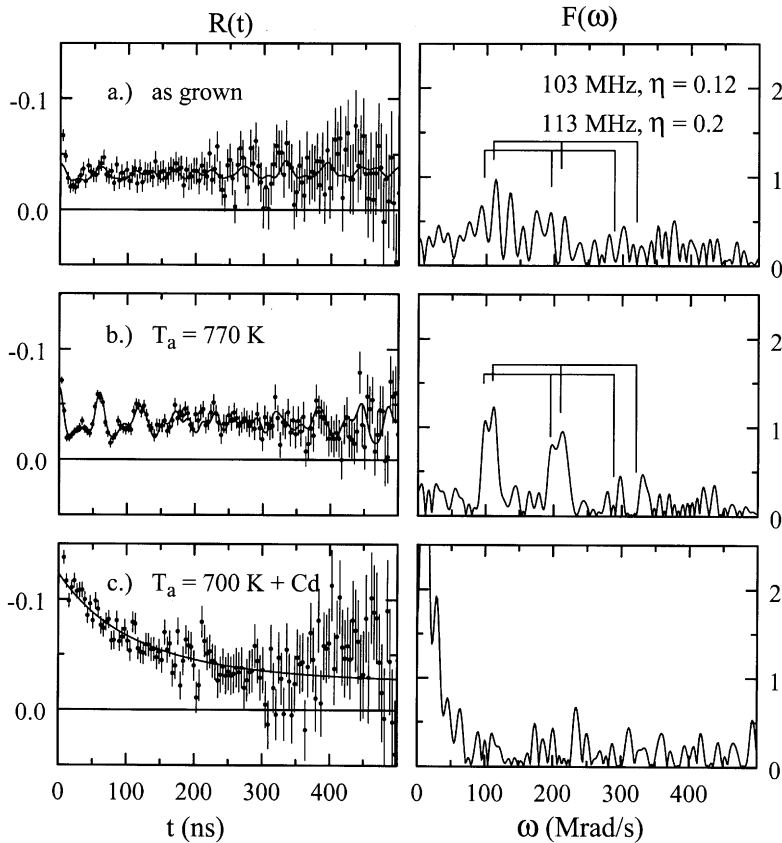


Fig. 2. PAC measurements of MOCVD grown CdTe epilayers doped in situ with ^{111}In at 663 K: (a) as grown, (b) annealed for 30 min at 770 K in vacuum, (c) annealed for 30 min at 700 K in Cd vapour.

As discussed before, now a much stronger incorporation of In into the layers occurred. The PAC data shown in Fig. 3a were obtained from a layer grown with a Te to Cd ratio of 3 : 1. The resulting In concentration in the layer was larger than 10^{22} cm^{-3} , as determined from the measured γ -activity of the layer. At the same time, the PAC data showed an EFG of 24 MHz, which is known to characterise ^{111}In in an InTe lattice [8]. If the Te to Cd ratio was reduced to 1 : 1, the PAC data showed an EFG of $\nu_Q = 17 \text{ MHz}$, $\eta = 0$ (Fig. 3b), which is typical for In metal [9], and indicate that the deposited layer contained extended precipitates of In-metal.

The crystalline quality of the CdTe layers doped with the TM^{111}In precursor was investigated by

PL measurements. As a reference, the PL-spectra of CdTe layers doped with commercially available high purity TMIIn are shown in Fig. 4a and b. The CdTe layer doped with less than 10^{18} cm^{-3} In donors was dominated by strong excitonic lines (Fig. 4a). In contrast, if the CdTe layer was doped with more than 10^{18} cm^{-3} In donors, the PL spectrum was dominated by a broad DAP band, which is assigned to the In-related A-centre [10]. A CdTe layer doped with the radioactive TM^{111}In precursor shows a PL spectrum (Fig. 4c), which is very similar to that of the CdTe crystal doped with more than 10^{18} In donors (Fig. 4b). If the layer was subsequently annealed at $T = 700 \text{ K}$ under Cd pressure, the PL spectrum in addition showed excitonic lines and the DAP band became more

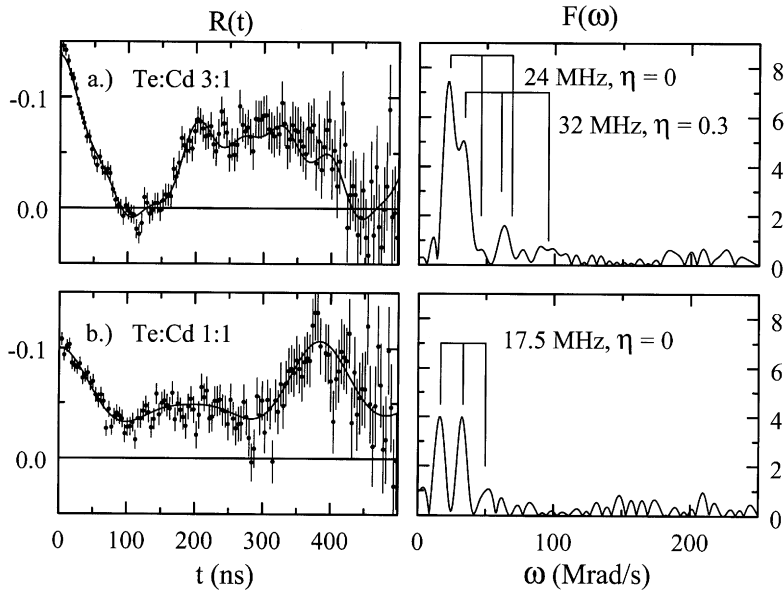


Fig. 3. PAC measurements of MOCVD grown CdTe layers doped in situ with ^{111}In at 703 K. Te : Cd ratio: (a) 3 : 1, (b) 1 : 1.

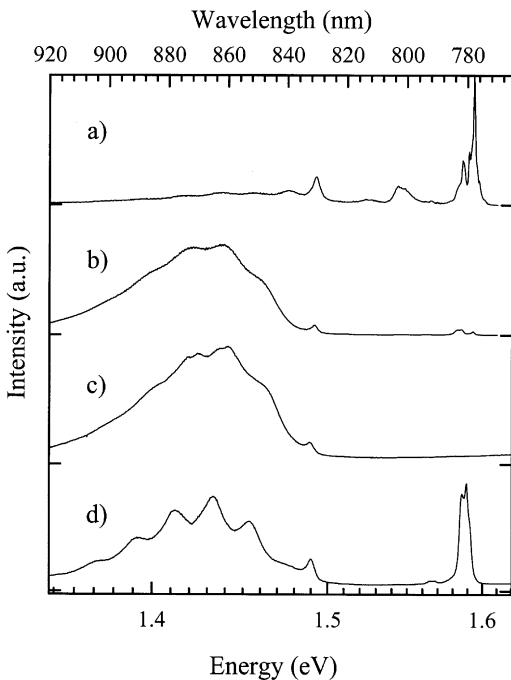


Fig. 4. PL-spectra of CdTe epilayers grown on GaAs: (a) In concentration $< 10^{18} \text{ cm}^{-3}$, (b) In concentration $> 10^{18} \text{ cm}^{-3}$, (c) doped in situ with ^{111}In , as grown and (d) after $T_A = 700 \text{ K}$, 30 min + Cd.

resolved. Obviously, the crystalline quality of the layer is significantly improved by annealing the layer under Cd pressure.

4. Summary and outlook

Radioactive ^{111}In dopant atoms, which are suitable as probes for PAC investigations and, at the same time, represent donor atoms in II–VI semiconductors, were incorporated into CdTe layers during MOCVD growth. At present, the used radioactive precursor TM^{111}In has to be supplemented by a stable carrier consisting of TMIIn . Experiments targeted towards a reduction of the ratio stable to radioactive In are in progress so that PAC probes can be placed at selected depths of the grown layer and the characterisation of narrow preselected regions of the grown layers by PAC should become feasible.

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