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Abstract. CdTe monocrystals were diffused with 10^{19} cm^{-3} In atoms at 800 °C in Cd vapour. The local environment of ^{111}Cd populated by the radioactive decay of the nuclide ^{111}In has been monitored with the time-differential perturbed angular-correlation method. The application of this technique provides the first direct information on the involvement of In-defect species in the compensation behaviour of highly doped CdTe. After quenching to room temperature, besides a substitutional fraction, two In-correlated complexes are found that involve interstitial or antisite defects. The complexes are formed and dissociate reversibly at 600 K. After slow oven cooling following the In diffusion, a third fraction is observed that is associated with InCd precipitates.

1. Introduction

Cadmium telluride is a compound semiconductor with cubic zincblende structure, i.e. each atom is surrounded by four tetrahedrally coordinated atoms of the other element, respectively. Among these IIB–VIA compounds, CdTe exhibits the highest ionicity and smallest band gap: $\Delta E = 1.60$ eV at 2 K (Strauss 1977). The electrical conductivity strongly depends on the concentration of intrinsic and impurity defects. Highly resistive CdTe is a very appropriate material for γ-ray detectors. Therefore, great effort was concentrated on obtaining an understanding of the complicated defect chemistry of CdTe (Watson and Shaw 1983, Selim *et al* 1975, Marfaing 1977, Kröger 1977).

Considerable interest has been focused on indium impurities, which on Cd sites act as donors. However, several experimental studies of the electrical properties of In-doped CdTe have revealed that the donors can be compensated to a degree that depends on the annealing temperature and vapour composition and on the cooling process (Selim *et al* 1975, Watson and Shaw 1983). This compensation is accompanied by the occurrence of several deep levels in the band gap (Ido *et al* 1987, Barnes and Zanio 1975). The particular role of In in CdTe was also detected in measurements of the diffusivity and solubility of In (Watson and Shaw 1983). After diffusion under Cd pressure, the In-concentration profile had to be described by the sum of two well discernible erfcs. This result indicates that In atoms are somehow involved in the formation of defect complexes, but up to now unequivocal evidence of how the In-correlated defects are formed in CdTe doped with In under Cd vapour has been lacking.

This paper reports the first experiments that are particularly appropriate to answer the above question concerning the role of In impurities in the compensation process. We employed the time-differential perturbed angular-correlation (TDPAC) technique. The perturbation of the angular-correlated γ–γ cascade of [111]Cd following the electron capture (EC) of a ^{111}In nucleus is due to the quadrupole interaction of the intermediate [111]Cd state with the electric field gradient (EFG) at the site of the nucleus. Thus, as a particular defect in the neighbourhood of a ^{111}In atom causes a unique EFG, the PAC method is very suitable for classifying the defect chemistry of In-doped CdTe.

This work provides information on the hyperfine parameters of the In complexes found. The results are compared with those of PAC and Mössbauer experiments on In-implanted CdTe (Kalish *et al* 1982, Grann *et al* 1986) and put into relation with the net electron concentration measured with the *C–V* method.

PAC experiments on the thermal stability, charge stability and annealing behaviour of In-correlated complexes in CdTe are the subject of a paper in preparation (Meyer *et al* 1989).

2. Experimental procedure

Radioactive ^{111}In populates the $\frac{7}{2}+$ [111]Cd level by EC. The nucleus decays via the isomeric $\frac{5}{2}+$ level to the $\frac{1}{2}+$ ground state. The two emitted γ quanta are angularly correlated according to

$$W(\Theta) = 1 - A_{22}P_2(\cos \Theta)$$

Where $W(\Theta)$ is the angularly dependent emission probability of the second γ quantum with respect to the first and $A_{22} = -0.176$ is the anisotropy coefficient. If the quadrupole moment ($Q = 0.77b$) of the nucleus interacts with an EFG during the lifetime of the intermediate state ($\tau = 122$ ns), the angular correlation is perturbed due to the quadrupole splitting. The time-dependent perturbation function is expressed by

$$G(t) = \sum_{n=0}^{3} s_n(\eta, \langle \text{EFG} \rangle) \cos(g_n(\eta)\nu_Q t) \exp(-g_n(\eta)\delta t)$$

where the quadrupole frequency $\nu_Q = eQV_{zz}/h$ is determined by the strongest component V_{zz} of the diagonalised EFG tensor. The coefficients g_n and s_n depend on the properties of the nuclear cascade and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ of the EFG tensor with $V_{xx} + V_{yy} + V_{zz} = 0$ (Laplace equation) and the setting $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Thus, η can vary between 0 (axial symmetry) and 1 (non-axiality). In the case of single crystals, the coefficients s_n are also functions of the EFG principal axes and detector orientations with respect to the crystal system (Wegner 1985). The exponential term in $G(t)$ accounts for a Lorentzian distribution of quadrupole frequencies around ν_Q which may be caused by a random lattice distortion. Note that at a probe-atom site with tetrahedral or octahedral atomic coordination the EFG vanishes and $G(t) = 1$. If relative fractions f_i of the probe atoms are exposed to different EFG with $G_i(t)$, the resulting perturbation function consists of the weighted mean $G(t) = \Sigma_i f_i G_i(t)$. The spectra were recorded by means of a conventional fast–slow coincidence set-up with

four NaJ detectors (total FWHM = 3.5 ns). From the simultaneously stored four 180° and eight 90° or 70°/110° spectra the function

$$R(t) = 2\frac{N(180°, t) - N(\Theta, t)}{N(180°, t) + 2N(\Theta, t)} \simeq A_{22}^{\text{eff}}G(t)$$

was calculated, where $N(180°, t)$ and $N(\Theta, t)(\Theta = 90°, (70°/110°))$ are the geometrical averages of equivalent original spectra corrected for background. The Fourier transform of the $R(t)$ function displays the frequencies $\omega_n = g_n(\eta)\nu_Q$ and amplitudes $s_n(\eta, \langle\text{EFG}\rangle)$ of the harmonics related with a particular perturbation.

The fits of the theoretical perturbation function were conducted with the computer code MINUIT (James and Roos 1977) and the coefficients s_n for monocrystal PAC measurements have been taken from Wegner (1985).

3. Sample preparation

A CdTe single crystal was grown following a modified Brigdman method under excess Cd vapour (Kyle 1971). Slices of 1.3 mm thickness were prepared from the rod. Their orientation was checked by Laue diffraction. C-V measurements revealed a net electron concentration of about 10^{14} cm^{-3}. The samples were mechanically polished using 1000-size grit and subsequently diamond paste down to 0.25 μm grain size. Prior to the indium diffusion they were chemically cleaned with a 3% solution of CH_3OHBr and finally put into an ultrasonic bath of 1n KOH–CH_3OH solution in order to remove a thin Te layer.

The quartz ampules with quartz-sample containers for the diffusion were etched twice in $1:1$ HF:H_2O and subsequently washed in bi-distilled water. Then they were outgassed at 1100 °C for some hours under a vacuum of less than 10^{-3} Pa. The diffusion source was made up from 5N Cd on which 5N indium was vapour-deposited to a mass ratio Cd/In of $4.6:1$. The ^{111}In activity (about 10^{12} atoms) was introduced either by implantation into the Cd/In foil with the Göttingen heavy-ion implanter IONAS (Uhrmacher *et al* 1985) or via the ^{111}Cd(d, 2n)^{111}In reaction by irradiation of Cd with the Göttingen synchro-cyclotron. The quartz ampule containing the CdTe sample and the Cd/In diffusion source was evacuated (10^{-3} Pa) and sealed. The diffusion temperature was 800°C and the duration 1 h. Then, according to Watson and Shaw (1983), the diffusion length of In from an alloy source is 32 μm and the surface concentration about 10^{19} cm^{-3}. The as-diffused state was conserved by quenching the ampule in ethylene glycol at room temperature. One sample container was slowly cooled in the oven. Another pure CdTe sample was directly implanted with ^{111}In ions.

In order to ensure that the In donors are mostly compensated, the net electron concentrations of identically doped samples were checked by depth-sensitive C-V measurements. Three ranges were distinguished (d = distance to the surface) as follows.

(i) $d > 190$ μm. The electron concentration is constant and equal to that of the non-doped samples.

(ii) $100 < d < 190$ μm. The concentration profile can be described by the solution of the diffusion equation $c(d, t) = c_0$ erfc$(d/2(D_{\text{In}})^{1/2}t)$, where erfc is the complementary error function and the fit parameters are the surface concentration $c_0 = 0.85(10) \times 10^{19}$ cm^{-3} and the diffusion constant of In, $D_{\text{In}} = 2.6(7) \times 10^{-9}$ cm^2 s^{-1}.

(iii) $d < 100$ μm. Again, the electron concentration is quite constant, namely $5(2) \times 10^{16}$ cm^{-3}.

Table 1. Parameters and fractions of the complexes observed in quenched (Q), slowly cooled (S) CdTe after In/Cd diffusion and in ^{111}In implanted CdTe (I).

Sample	Complex	f (%)	ν_Q (MHz)	δ (MHz)	η	$\langle$EFG$\rangle$ z axis
Q, S	'0'	23–36	0	<0.5	—	—
I	'0'	76	0	8.5(5)	—	—
Q, S	1	34–50	100(2)	1.5(5)	<0.05	$\langle 111 \rangle$
Q, S	2	26–42	111(2)	<1	0.18(2)	$\langle 111 \rangle$
S, Q + I + Q	3	26	16.1(5)	4.3(10)	0	Random
I	4	24	115(1)	2.0(2)	0	—

A comparison of these results with the data of Watson and Shaw (1983) reveals that the erfc profile of range (ii) represents the concentration of In atoms. The values of both c_0 and D_{In} agree, within their errors. The conclusion is that for In concentrations higher than some 10^{16} cm^{-3} compensation dominates the electronic-donor activity. In and donor concentrations at the surface differ by more than two orders of magnitude.

4. Results

The results of our experiments are listed in table 1. After diffusion of In under Cd pressure, three EFG could be distinguished, with the hyperfine parameters $\nu_{Q0} = 0$, $\delta_0 < 0.5$ MHz, $\nu_{q1} = 100(2)$ MHz, $\delta_1 = 1.5(5)$ MHz, $\eta_1 < 0.05$ and $\nu_{Q2} = 111(2)$ MHz, $\delta_2 < 1$ MHz, $\eta_2 = 0.18(2)$. Typical perturbation functions and Fourier transforms are shown in figure 1. The figure displays the results for three different detector orientations and nicely demonstrates that the EFG z axes of complexes 1 and 2 both point along a $\langle 111 \rangle$ crystallographic axis (Wegner 1985). The fractions of the complexes vary as $f_0 = 23$–36%, $f_1 = 34$–50% and $f_2 = 21$–42%. These variations and the errors of the parameters do not reflect the statistical inaccuracy of the measurements but are due to differences between the samples. This is demonstrated in figure 2, which shows a correlation between $\nu_{Q1,2}$ and f_2 respectively $f_2 + f_3$ if $f_3 \neq 0$ (for f_3 see below). A similar dependence of the quadrupole frequencies on the fractions emerges from the temperature variation. Complexes 1 and 2 are stable up to about 600 K. The formation and dissociation processes are reversible. The disintegration of the complexes is accompanied by a significant decrease of the quadrupole frequencies by some MHz. This has to be considered as a macroscopic effect because the variations of ν_{Q1} and ν_{Q2} are strongly correlated.

The oven-cooled sample exhibited a relatively small fraction, $f_0 = 18\%$, but in addition a third PAC contribution was found with the fraction $f_3 = 26\%$ and the parameters $\nu_{Q3} = 16.1(5)$ MHz, $\delta_3 = 4.3(10)$ MHz, $\eta_3 = 0$ (figure 3a). The related EFG was randomly oriented.

After implantation of ^{111}In into pure CdTe, a broad distribution of EFG around zero ($f_0 = 76\%$) and a further complex 4 ($f_4 = 24\%$) with $\nu_{Q4} = 115(1)$ MHz, $\delta_4 = 2.0(2)$ MHz and $\eta_4 < 0.1$ was observed (figure 3c). The accuracy of the frequency allows complex 4 to be discerned from complex 2. After implantation of ^{111}In into CdTe, Kalish *et al* (1982) found the same perturbation. In contrast to complex 2, which is thermally stable at
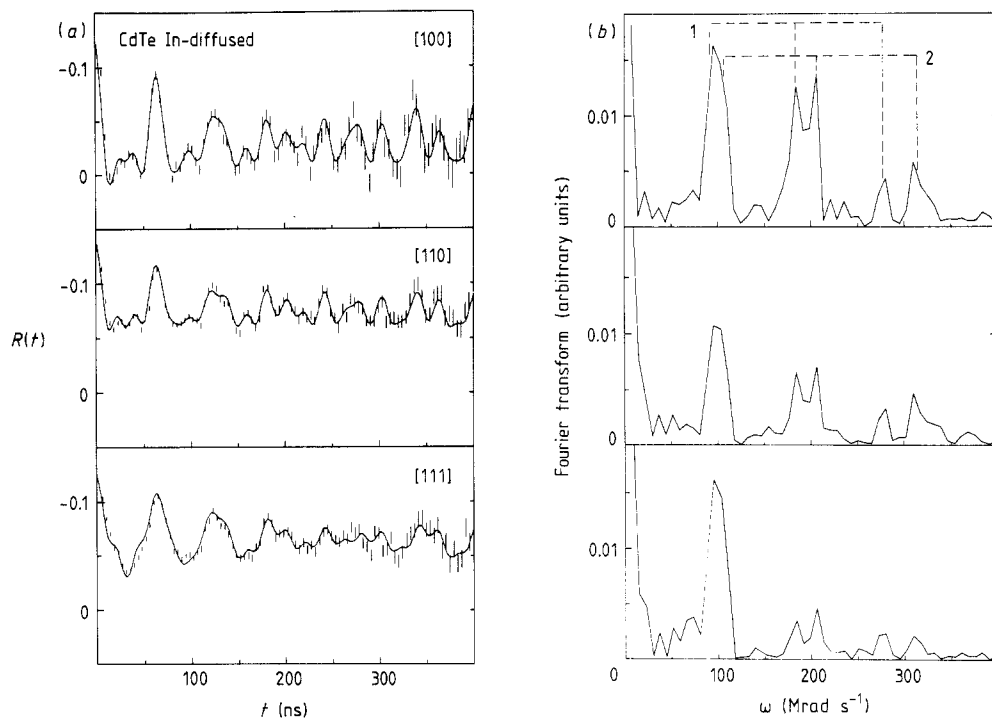
Figure 1. (*a*) Perturbation functions $R(t)$ and (*b*) Fourier transforms with fractions 0–2 measured with detectors oriented along [100], [110] and [110] crystallographic directions. The dotted lines indicate the harmonics of perturbation factors 1 and 2.
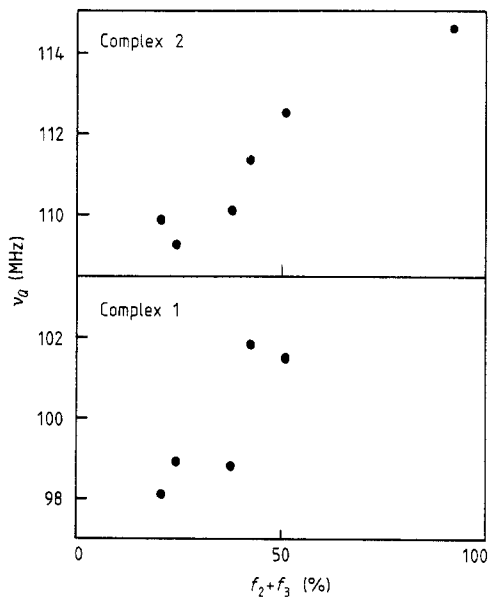
Figure 2. Quadrupole frequencies ν_{Q1} and ν_{Q2} as a function of the fraction or f_2 ($f_2 + f_3$) if $f_3 \neq 0$.
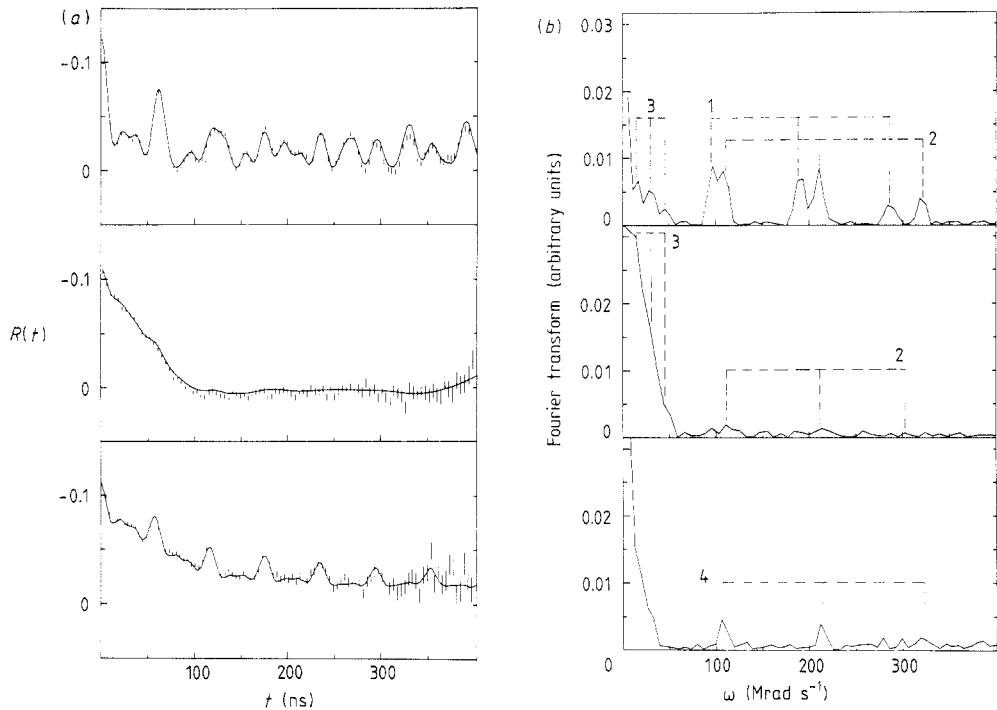
Figure 3. Typical (*a*) perturbation functions $R(t)$ and (*b*) Fourier transforms for an (top) In-diffused and oven-cooled sample; (middle) In diffused, ^{111}In implanted and 2 min at 800 °C annealed sample; (bottom) [111]In implanted undoped CdTe sample.

600 K, the implantation-induced defect 4 starts to decay after vacuum annealing at 375 K (Kalish *et al* 1982).

5. Discussion

In the foregoing section we outlined the result that, after the doping of CdTe with In under Cd pressure, three or, after slow cooling, four different electrical In environments can be observed with PAC. Irrespective of the important question of how the results have to be interpreted in detail, we wish to emphasise the following. The experiments have unambiguously proven that the electronic compensation of highly In-doped CdTe occurs essentially by the formation of In-correlated defects. This means, in particular, that any compensation model dealing with self-compensation solely via intrinsic defects or defect complexes is inadequate. Of course, intrinsic defects may play an important role but they are not accessible to the PAC method.

The symmetry of the zincblende structure predicts a vanishing EFG for substitutional lattice sites. Thus 'complex 0' can be attributed to substitutional ^{111}In atoms on Cd sites. In_{Cd} is a single donor and, therefore, at least one of the complexes 1 and 2 is neutral or even acceptor-like. The thermal stability of the frequencies over a wide range of temperatures hints at a constant-charge state. Thus both defects are not shallow donors or acceptors (Witthuhn 1985). As we have no information on the concentration of intrinsic defects, more precise statements concerning the charge of the defects are impossible on the basis of this work.

The quadrupole frequencies $\nu_{Q1,2}$ measured cannot be interpreted as ^{111}In in Cd, In, Te, InTe, In_2Te_5, β-In_2Te_3 precipitates (Vianden 1987, Frank *et al* 1987, Forkel *et al* 1983). The sharp quadrupole frequencies, the (nearly) axial EFG symmetry and the (111) EFG axis orientations of complexes 1 and 2 indicate that only point defects are involved. We can exclude only *one* complex with two In atoms on non-equivalent sites being the cause of both perturbations (e.g. In_{Cd}–In_{Te}) because the condition $f_1 = f_2$ is not generally fulfilled. We can also exclude the $^{111}In_{Cd}$–V_{Cd} structure which exhibits the hyperfine parameters $\nu_Q = 60$ MHz, $\eta = 0.19$ (Kalish *et al* 1982) and (110) axial symmetry. We were able to reproduce the ^{111}In–V_{Cd} complex by Cd evaporation in vacuum. If we take into account (i) that the formation of Te_{Cd} and Te_i is unlikely, due to the Cd diffusion atmosphere, (ii) that In_{Cd}^+ donors are attractive only for neutral or acceptor-like intrinsic defects and (iii) the (111) symmetry axes of complexes 1 and 2, the following configurations are likely: In_i–V_{Cd}, In_{Cd}–Cd_{Te}; In_i–Cd_{Te}, In_{Te}–Cd_i. One common property of all proposed defects is that they contain an interstitial and/or anti-site atom. Higher coordinated complexes with In atoms on equivalent sites are also conceivable, e.g. In_{Cd}–Cd_{Te}–In_{Cd}. This configuration has been proposed by Ido *et al* (1987) in order to explain the superlinear concentration dependence of an acceptor-like defect upon the In doping level. It would cause a slightly non-axial EFG and could serve as nucleus for In–Cd precipitates, which have been observed by Selim *et al* (1975).

This leads us to the discussion of complex 3. We tentatively attribute this perturbation to small In precipitates. The slow cooling after which f_3 was observed may have favoured the motion and precipitation of excess atoms. This interpretation would explain the random orientation of the related EFG. Furthermore, $\nu_{Q3} = 16.1$ MHz is very similar to the frequency of ^{111}Cd in pure In $\nu_Q = 17.3$ MHz (Vianden 1987). In that case, the width δ_3 of the distribution is due to the distortion of the small precipitates as a consequence of their structural misfit. We checked the hypothesis by an additional experiment in which a CdTe sample already diffused with In was implanted with ^{111}In. This procedure increases the In concentration in the implantation profile by a factor of 2 and should favour the formation of In precipitates. Indeed, after 2 min annealing at 800 °C in Cd/In atmosphere we found a large f_3 (figure 3*b*).

Figure 2 shows that the lower the fraction f_2, the lower the quadrupole frequencies ν_{Q2} and ν_{Q3}. The decrease of f_2 and f_3 enlarges f_1 and thus the net carrier concentration. In a simple model the EFG at a nucleus can be expressed by a sum of an ionic and an electronic contribution. The latter is caused by polarisation of the conduction electrons and depends on the free-electron density (Witthuhn 1985). This picture gives an understanding of why the frequencies vary with the fractions and hints at complex 2 being an acceptor-type defect.

The question of the structure of complex 4 remains open. Applying a Mössbauer emission spectroscopy of ^{119}Sn after implantation of ^{119m}Cd or ^{119}In into CdTe, Graun *et al* (1986) found a defect which they attributed to Cd_{Cd}–V_{Te} and In_{Cd}–V_{Te} respectively and identified with the $\nu_Q = 115$ MHz complex reported by Kalish *et al* (1982) and in this work. The configuration is produced athermally by In recoil and dissociates if the Te vacancy becomes mobile. We measured the perturbation function of complex 4 along the (100) crystallographic orientation and found consistence with a (111) axial symmetry of the EFG, which was only to be expected.

6. Summary

This is the first experiment that directly proves the existence of In-correlated defects at room temperature in highly doped CdTe : In. The complexes observed with the hyperfine

parameters $\nu_{Q1} = 100(2)$ MHz, $\eta_1 \approx 0$ and $\nu_{Q2} = 111(2)$ MHz, $\eta_2 = 0.18(2)$ and $\langle 111 \rangle$ symmetry axes are stable up to about 600 K. The variation of the quadrupole frequencies with fraction f_2 can be understood in terms of the net electron concentration and indicates that at least complex 2 is acceptor-type. All configurations that may be proposed on the basis of the experimental findings involve an interstitial and/or anti-site defect. In one sample, slowly cooled after the In diffusion a fraction with $\nu_{Q3} = 16.1(5)$ MHz, $\eta_3 = 0$, was observed that was attributed to **InCd** precipitates. A complex with $\nu_{Q4} = 115(1)$ MHz, $\eta_4 = 0$ reported earlier by Kalish *et al* (1982) is observed after ^{111}In implantation. It is different from complex 2 with similar parameters and tentatively associated with the In_{Cd}–V_{Te} defect.

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