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Defect complexes induced by diffusion of group I acceptors into CdTe

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Abstract

The formation of defects following the diffusion of the group I acceptors Cu, Ag, or Au into CdTe was investigated by perturbed $\gamma\gamma$-angular correlation (PAC) using the radioactive donor $^{111}In_{Cd}$. The formation of A-centres (In_{Cd}–V_{Cd} pairs) with the donor $^{111}In_{Cd}$ was observed, indicating that the incorporation of the group I acceptors Cu, Ag, or Au is accompanied by the generation of cation vacancies. In addition, the formation of In_{Cd}–Ag_{Cd} or In_{Cd}–Au_{Cd} pairs was observed in CdTe. The concentration of cation vacancies formed after diffusion of Cu, Ag, or Au was found to depend only weakly on the respective group I element. In contrast, the migration energy of the cation vacancy was observed to be different in CdTe crystals doped with Ag or Au, yielding 0.76 (3) eV and 0.84 (3) eV, respectively. In Ag-doped CdTe the binding energies of the In_{Cd}–V_{Cd} pair and the In_{Cd}–Ag_{Cd} pair were determined to 0.18 (2) eV and 0.19 (2) eV, respectively. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Group I elements act as acceptors in CdTe if they are incorporated on Cd sites. The p-type conductivity of CdTe, however, that is achieved by doping with group I elements is strongly limited, yielding e.g. for Ag a maximum hole concentration of 2×10^{16} cm^{-3} [1], although the solubility of Ag is much higher. An effective p-type doping by group I elements may be prevented by the formation of compensating intrinsic defects or by the incorporation of group I elements also at interstitial lattice sites, acting there as donors. Thus, Chamonal et al. and Monemar et al. [2,3] proposed that close pairs of substitutional Ag_{Cd} acceptors and Ag_i donors are formed that passivate each other.

The formation of defect complexes upon doping of CdTe with group I acceptors was investigated by perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC) using the radioactive donor $^{111}In_{Cd}$, which decays to the host atom ^{111}Cd. The PAC data yield information about acceptor-like defects, which form complexes with the donor probe $^{111}In_{Cd}$. Besides the group I acceptors, the acceptor-like cation vacancy is detected by PAC in CdTe. The migration energies of acceptor defects and the binding energies of defect complexes are determined by annealing the crystals after quenching and by variation of the sample temperature.

2. Experimental procedure

The ^{111}In probe atoms were diffused into the CdTe crystals at temperatures between 800 and 970 K for times between 1.5 and 8 h. The total number of ^{111}In atoms/crystal was about 10^{12}, the diffusion length L_{In} was between 3.5 and 14 μm depending on the individual diffusion conditions (see Table 1). The resulting maximum concentration of ^{111}In atoms was about 10^{15} cm^{-3} after diffusion and decreased well below

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Table 1
Diffusion lengths $L = \sqrt{Dt}$ of the dopants [9] and site fractions f of the ^{111}In probe atoms at 295 K in thermal equilibrium

Dopant	L_{In} (µm)	L_A	f_c (%)	f_{In-V} (%)	f_{In-A} (%)
^{111}In	14	—	77	15	
^{111}In + Ag[a]	3.5	0.5 mm[c]	17	10	30
^{111}In + Ag[b]	3.5	0.5 mm[c]	31	26	17
^{111}In + Au	13	12 µm	55	38	—[d]
^{111}In + Cu	4	50 µm	25	46	—

[a] Variation of the measuring temperature (see Fig. 1).
[b] Annealing at 295 K (see Fig. 2a).
[c] Homogeneous distribution over the entire crystal assumed.
[d] Observable under altered diffusion conditions.

10^{15} cm^{-3} in the course of the experiments due to the radioactive decay.

For doping with Cu, Ag, or Au, a layer of 10 nm of the respective metal was evaporated onto the CdTe surface followed by a subsequent diffusion into the CdTe crystal. Since the metal layer on the surface represents an infinite diffusion source, the diffusion profile is described by the complementary error function, whereby the concentration at the surface is determined by the solubility. The diffusion lengths L_A of the group I dopants in the investigated crystals are listed in Table 1. As a reference, a CdTe crystal was diffused exclusively with ^{111}In at 860 K for 8 h and additionally treated at 1000 K for 10 min under Te pressure in order to generate cation vacancies.

In a PAC experiment, the site fractions of the probe atoms in specific local configurations are quantitatively detected. In the present experiments, the environment of ^{111}In probe atoms located on Cd lattice sites is of interest: whether they are incorporated isolated as electrically active donors or bound in pairs with either the cation vacancy V_{Cd} or the group I acceptors Ag_{Cd}, Au_{Cd}, or Cu_{Cd}. The different local configurations are distinguished by different electric field gradients (EFG), which are measured by PAC at the daughter isotope ^{111}Cd. The EFG tensor is usually expressed by the quadrupole coupling constant $v_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. A detailed description of PAC spectroscopy in semiconductors can be found in the literature [4].

3. Results

In CdTe crystals exclusively doped with ^{111}In, the formation of ^{111}In$_{Cd}$–V$_{Cd}$ pairs is [5–7] observed after heating the crystal at 860 K under Te pressure. The presence of the cation vacancies is recognised by the

EFG, characterised by $v_Q = 60.2$ (5) MHz and $\eta = 0.17$ (1). From the ^{111}In$_{Cd}$ donors, the fraction $f_{In-V} = 15\%$ have formed In$_{Cd}$–V$_{Cd}$ pairs and the fraction $f_c = 77\%$ are located on isolated Cd sites with cubic symmetry.

After diffusion of Cu, Ag, or Au into CdTe, the same EFG is observed; the fractions of In$_{Cd}$–V$_{Cd}$ pairs, however, are often significantly larger than after thermal treatment under Te pressure. The diffusion of group I elements into CdTe obviously enhances the formation of cation vacancies. In case of Ag or Au diffusion, under suitable conditions a second EFG is observed, which is slightly smaller than the EFG corresponding to the cation vacancy and is assigned to the donor–acceptor pairs In$_{Cd}$–Ag$_{Cd}$ ($v_Q = 56.6$ (5) MHz, $\eta = 0.11$ (2)) or In$_{Cd}$–Au$_{Cd}$ ($v_Q = 54.2$ (5) MHz, $\eta = 0.07$ (2)), respectively. In contrast, after diffusion of Cu a second EFG is not observable, suggesting that no In$_{Cd}$–Cu$_{Cd}$ pairs have been formed. The assignment of the detected EFG to these defect complexes will be discussed at an other place [8]. The present study focuses on the formation of In$_{Cd}$–V$_{Cd}$ pairs (A-centres) accompanying the diffusion of Ag, Au, or Cu and, especially, on the mobility of the cation vacancy V_{Cd} and the stability of the A-centres formed with ^{111}In$_{Cd}$ donors. In addition, the stability of the In$_{Cd}$–Ag$_{Cd}$ pair is determined. The diffusion lengths of the dopants in the investigated samples are calculated on the basis of published data [9] and are listed in Table 1.

3.1. CdTe : Ag

Two ^{111}In-doped CdTe crystals were diffused with Ag at 550 K for 60 min. Based on the high mobility reported for Ag in CdTe [10], a homogeneous distribution of the Ag atoms over the entire crystal is assumed with a concentration of [Ag] = 10^{18} cm^{-3}. After diffusion, the first sample was cooled to 295 K and subsequently measured at different temperatures in the range 295–550 K. The PAC data at 295 K show the ^{111}In atoms to be located at lattice sites with cubic symmetry, bound in ^{111}In$_{Cd}$–V$_{Cd}$ pairs, and in ^{111}In$_{Cd}$–Ag$_{Cd}$ pairs with the fractions $f_c = 17\%$, $f_{In-V} = 10\%$, and $f_{In-Ag} = 30\%$, respectively. Increasing the sample temperature, f_{In-V} and f_{In-Ag} decrease, and f_c increases, whereas the sum $f_{tot} = f_c + f_{In-V} + f_{In-Ag} = 57\%$ remains constant. The ratios f_{In-V}/f_c and f_{In-Ag}/f_c (see. Eq. (3a) and (3b) below) are plotted as a function of the temperature in Fig. 1 in an Arrhenius plot. The second crystal was heated to 800 K, quenched to 260 K with a cooling rate of about 10^3 K/s, and immediately transferred into a LN$_2$ bath. The PAC data show that following the quench In$_{Cd}$–Ag$_{Cd}$ pairs, but almost no In$_{Cd}$–V$_{Cd}$ pairs are formed [11]. The In$_{Cd}$–V$_{Cd}$ pairs are formed after annealing the crystal at 295 K. The fraction $f_{In-V}(t)$ measured within an isothermal annealing program is plotted in Fig. 2a. At the same time, the fraction of In$_{Cd}$–Ag$_{Cd}$ pairs only slightly increases from

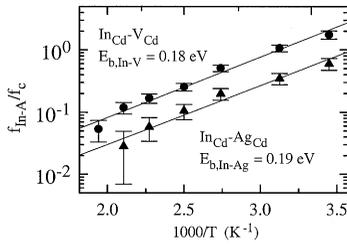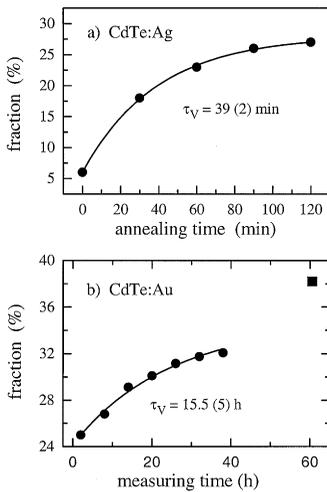Fig. 1. Arrhenius plot of the ratio $f_{\text{In-V}}/f_c$ and $f_{\text{In-Ag}}/f_c$ in CdTe diffused with Ag.

Fig. 2. Fraction of In_{Cd}–V_{Cd} pairs in (a) CdTe : Ag as a function of the annealing time at 295 K and (b) in CdTe : Au as a function of the accumulated measuring time. The last data point (square at 60 h) was taken after re-starting the measurement.

14% to 17%. The increase of the fraction of A-centres is well described by an exponential law with a time constant of $\tau_V = 39$ min (solid line in Fig. 2a). The time constant agrees fairly well with the time constant reported by Reislöhner et al. for the formation of $^{111}\text{In}_{\text{Cd}}$–$\text{V}_{\text{Cd}}$ pairs after dipping a CdTe crystal in an aqueous solution of AgNO_3 [12].

3.2. CdTe : Au

An ^{111}In doped CdTe crystal was diffused with Au for 60 min at 900 K. The resulting diffusion lengths of the ^{111}In and the Au atoms were nearly identical (see Table 1). In this case, no In_{Cd}–Au_{Cd} pairs are formed, whereas the formation of In_{Cd}–V_{Cd} pairs is observed at ambient temperature like in the case of Ag. The time constant τ_V, however,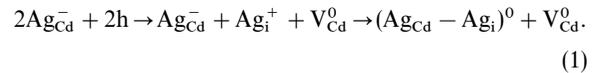 is significantly larger than in the Ag-diffused sample. For practical reasons the experimental procedure was modified. After diffusion of Au, the crystal was measured at ambient temperature over a longer time, whereby the data were stored in time intervals of 6 h. The fraction of A-centres as a function of the accumulated measuring time is plotted in Fig. 2b. For the last data point (60 h after Au diffusion; square) the measurement was re-started, in this way yielding the equilibrium value of the fraction of In_{Cd}–V_{Cd} pairs, $f_{\text{In-V}} = 38\%$ directly.

3.3. CdTe : Cu

After diffusion of Cu into CdTe doped with ^{111}In, the formation of A-centres at ambient temperature happens faster than in case of Ag diffusion. The PAC data show that at thermal equilibrium $f_{\text{In-V}} = 46\%$ of the $^{111}\text{In}_{\text{Cd}}$ donors are bound in In_{Cd}–V_{Cd} pairs and $f_c = 25\%$ remained at lattice sites with cubic symmetry (see Table 1).

4. Discussion

A mechanism of the compensation of group I acceptors, involving the formation of cation vacancies V_{Cd}, is described by the defect reaction (e.g. for the Ag_{Cd} acceptor)

$$2\text{Ag}_{\text{Cd}}^- + 2h \rightarrow \text{Ag}_{\text{Cd}}^- + \text{Ag}_i^+ + \text{V}_{\text{Cd}}^0 \rightarrow (\text{Ag}_{\text{Cd}} - \text{Ag}_i)^0 + \text{V}_{\text{Cd}}^0. \tag{1}$$

It describes the conversion of the shallow level of the Ag_{Cd} acceptor into deep levels of the double acceptor defect V_{Cd}. Simultaneously, electrically inactive $(\text{Ag}_{\text{Cd}}\text{-Ag}_i)$ pairs are formed as proposed by Chamonal et al. and by Monemar et al. [2,3]. The cation vacancies may be trapped at the surface of the crystal or at donor-like defects. The trapping at the radioactive donor $^{111}\text{In}_{\text{Cd}}$ enables the direct detection by PAC. Additionally, the $^{111}\text{In}_{\text{Cd}}$ donors form complexes with Ag_{Cd} acceptors that are not bound in $\text{Ag}_{\text{Cd}}\text{-Ag}_i$ pairs.

The formation of close pairs of the $^{111}\text{In}_{\text{Cd}}$ donor with two different acceptor defects $A_{\text{Cd},1}$ and $A_{\text{Cd},2}$ during an annealing experiment is described by coupled rate equations. If the concentrations of the acceptor defects $[A_{\text{Cd},k}]$ significantly exceed the total concentration of the involved ^{111}In atoms $[\text{In}_{\text{Cd}}]_{\text{tot}}$, as is the case in the present experiments, the rate equations are

$$\frac{\text{d}}{\text{d}t}[\text{In}_{\text{Cd}} - A_{\text{Cd},k}] = -\lambda_k[\text{In}_{\text{Cd}} - A_{\text{Cd},k}]$$
$$+ \mu_k[A_{\text{Cd},k}][\text{In}_{\text{Cd}}] \quad (k = 1, 2) \tag{2}$$

with

$$\lambda_k = \nu_{0,k}\exp(-(E_{\text{m},k} + E_{\text{b},k})/kT),$$
$$\mu_k = \nu_{0,k}\Omega_k\exp(-E_{\text{m},k}/kT),$$

and

$$[\text{In}_{\text{Cd}}]_{\text{tot}} = [\text{In}_{\text{Cd}}] + [\text{In}_{\text{Cd}} - A_{\text{Cd},1}] + [\text{In}_{\text{Cd}} - A_{\text{Cd},2}].$$

The decrease of $[\text{In}_{\text{Cd}}]_{\text{tot}}$ due to the radioactive decay can be separated from Eq. (2). Since in the following only the fractions of In atoms in specific configurations are of interest, $[\text{In}_{\text{Cd}}]_{\text{tot}}$ can be treated as constant. The rates of dissociation (λ_k) and formation (μ_k) depend on specific properties of the involved acceptor defects $A_{\text{Cd},k}$, like the attempt frequency $v_{0,k}$ and the migration energy $E_{\text{m},k}$. The trapping volume Ω_k and the binding energy $E_{\text{b},k}$ are properties of the defect complexes $\text{In}_{\text{Cd}} - A_{\text{Cd},k}$. In general, the fractions $f_{\text{In}-k}(t)$ of $^{111}\text{In}_{\text{Cd}}$ donors bound at the time t in the defect complexes $\text{In}_{\text{Cd}} - A_{\text{Cd},k}$ are obtained by integrating the time -dependent solutions of Eq. (2) over the entire crystal and dividing the result by the total number of ^{111}In atoms. For the interpretation of the present data, however, only some special solutions are of interest.

4.1. CdTe : Ag

Since the concentrations of both defect complexes are in thermal equilibrium in the experiments shown in Fig. 1, the following solutions of the rate equations (Eq. (2)) are obtained

$$f_{\text{In}-V}/f_c = \Omega_V[\text{V}_{\text{Cd}}]\exp(E_{\text{b},\text{In}-V}/kT) \qquad (3a)$$

and

$$f_{\text{In}-\text{Ag}}/f_c = \Omega_{\text{Ag}}[\text{Ag}_{\text{Cd}}]\exp(E_{\text{b},\text{In}-\text{Ag}}/kT), \qquad (3b)$$

giving direct access to the binding energies of both defect complexes. The experimental data yield for the binding energies of the $\text{In}_{\text{Cd}} - \text{V}_{\text{Cd}}$ pair and the $\text{In}_{\text{Cd}} - \text{Ag}_{\text{Cd}}$ pair $E_{\text{b},\text{In}-V} = 0.18\,(2)\,\text{eV}$ and $E_{\text{b},\text{In}-\text{Ag}} = 0.19\,(2)\,\text{eV}$, respectively, as well as $\Omega_V \cdot [\text{V}_{\text{Cd}}] = 4.6 \times 10^{-4}$ and $\Omega_{\text{Ag}} \cdot [\text{Ag}_{\text{Cd}}] = 1.0 \times 10^{-3}$. The binding energy of the $\text{In}_{\text{Cd}} - \text{V}_{\text{Cd}}$ pair is somewhat larger than the value of 0.15 (1) eV reported by Griffith et al. [7], what, however, might be connected with the fact that a powder sample was used instead of a single crystal.

During the isothermal annealing experiment at 295 K, the fraction of $\text{In}_{\text{Cd}} - \text{Ag}_{\text{Cd}}$ pairs remained almost constant, indicating that the concentration of the $\text{In}_{\text{Cd}} - \text{Ag}_{\text{Cd}}$ pairs was in thermal equilibrium. The time constant τ_V, which describes the formation of the $\text{In}_{\text{Cd}} - \text{V}_{\text{Cd}}$ pairs, is consequently mainly governed by the migration energy of the cation vacancy and is well approximated by

$$1/\tau_V = v_{0,V}\exp(-E_{\text{m},V}/kT)$$
$$\times (\Omega_V[\text{V}_{\text{Cd}}] + \exp(-E_{\text{b},\text{In}-V}/kT)). \qquad (4)$$

From this equation the migration energy $E_{\text{m},V}$ of V_{Cd} is extracted. Using the values of $E_{\text{b},\text{In}-V}$ and $\Omega_V \cdot [\text{V}_{\text{Cd}}]$ determined above, the attempt frequency 10^{12} $\text{s}^{-1} < v_{0,V} < 10^{13}\,\text{s}^{-1}$, which is typical for phonon fre-

quencies in solids, and the experimentally determined time constant of $\tau_V = 39$ min (Fig. 2a), the migration energy $E_{\text{m},V} = 0.76(3)\,\text{eV}$ is deduced. This value is slightly smaller than the energy of 0.80 (5) eV reported in Ref. [11], using simplified assumptions for $\Omega_V \cdot [\text{V}_{\text{Cd}}]$ and a more simple model.

4.2. CdTe : Au

Since no $\text{In}_{\text{Cd}} - \text{Au}_{\text{Cd}}$ pairs are observed during the isothermal annealing sequence (Fig. 2b), the formation of $\text{In}_{\text{Cd}} - \text{V}_{\text{Cd}}$ pairs is described by a single rate equation. With regard to the evaluation of the time constant τ_V, two remarks have to be made. Firstly, the profile of V_{Cd} is assumed to be constant, which actually does not seem to be realistic because the diffusion length of the Au dopant is nearly identical with that of the ^{111}In dopant. Therefore, the time constant τ_V and consequently the expression $\Omega_V[\text{V}_{\text{Cd}}]$, have to be regarded as values averaged over the diffusion profiles. Secondly, it has to be considered that the fraction of $\text{In}_{\text{Cd}} - \text{V}_{\text{Cd}}$ pairs $f_{\text{In}-V}(t)$ increases continuously during the PAC measurement and, at the same time, the counting rate decreases due to the radioactive decay of the ^{111}In atoms. The time dependent solution of the rate equation

$$f_{\text{In}-V}(t) = f_{\text{In}-V} + (f_{\text{In}-V,0} - f_{\text{In}-V})(1 - \exp(-t/\tau_V)), \qquad (5)$$

therefore, has to be averaged over the measuring time, which, however, can be treated exactly. The symbols $f_{\text{In}-V,0}$ and $f_{\text{In}-V}$ denote the fraction of $\text{In}_{\text{Cd}} - \text{V}_{\text{Cd}}$ pairs at the beginning of the measurement and at thermal equilibrium, respectively. The fraction $f_{\text{In}-V}$ was determined by starting a new measurement (square in Fig. 2b). From the experimental data, the time constant $\tau_V = 15.5(5)$ h and the fraction of $f_{\text{In}-V,0} = 24\%$ at the beginning of the experiment is determined (solid line in Fig. 2b). The ratio $f_{\text{In}-V}/f_c = 0.69$ is close to that observed at 295 K after Ag diffusion ($f_{\text{In}-V}/f_c = 0.59$), suggesting that the concentration of V_{Cd} is almost the same after Au and Ag diffusion. Since the attempt frequency $v_{0,V}$ is a property of the CdTe lattice, and Ω_V and $E_{\text{b},\text{In}-V}$ are local properties of the $\text{In}_{\text{Cd}} - \text{V}_{\text{Cd}}$ pair, the different time constants τ_V observed after Ag and Au diffusion can only be explained if the migration energy $E_{\text{m},V}$ is different (see Eq. (4)). The extracted migration energy of the V_{Cd} defect in the Au-doped CdTe crystal is determined to be $E_{\text{m},V} = 0.84(3)\,\text{eV}$, as compared to 0.76 (3) eV in the Ag-doped crystal.

4.3. CdTe : Cu

From the present experimental data the migration energy of the cation vacancy cannot be determined. The ratio $f_{\text{In}-V}/f_c = 1.82$, however, is in the same order of magnitude as obtained after Ag or Au diffusion. Thus, the

concentration of V_{Cd} is obviously close to that observed after Ag or Au diffusion. It is suggested that at high concentration of the group I dopants the concentration of V_{Cd} is governed by intrinsic properties of CdTe.

5. Conclusion

In CdTe crystals, doped with the group I acceptors Ag, Au, or Cu, the formation of A-centres was investigated by PAC. The mobility of the cation vacancy V_{Cd} is different after diffusion of Ag or Au, whereas the concentration of the formed cation vacancies varies only slightly. Since the mobility of the cation vacancy can be affected by the presence of dopants, the observed differences might indicate different concentrations of the group I dopants. By Griffith et al. the mobility of the cation vacancy was observed in CdTe doped exclusively with ^{111}In. There, the mobility was significantly lower than in the present experiments. The lower mobility may be connected with the use of a powder sample, giving rise to a higher defect concentration. In contrast, the present experiments show that the concentration of the generated cation vacancies does not significantly depend on the nature of the introduced group I dopant Cu, Ag, or Au, nor on its concentration.

Acknowledgements

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