

The Role of Intrinsic Defects for the Diffusion of Ag and Cu in CdTe

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Abstract. Ag and Cu diffused into CdTe exhibit unusual shapes of their concentration profiles, especially if the diffusion was performed under Cd vapor pressure. The shapes of the concentration profiles at low concentrations of Ag or Cu are well described by a model based on the interaction with intrinsic defects. In that model the characteristic features of the profiles can be independently reproduced by appropriate parameters. It turns out that the resulting profiles are determined by the diffusion of interstitial Cd atoms and reflect the actual distribution of the intrinsic defects in the crystal, i.e. the deviation from stoichiometry.

Introduction

The electrical and optical properties of semiconductors are essentially determined by the presence of donor and acceptor atoms. The group I elements Ag and Cu are known as substitutional acceptors in CdTe, but the hole concentration achieved by doping with Ag or Cu is much lower than the corresponding concentration of group I atoms. In addition, both elements are reported to be incorporated as interstitial donors and the mobility of interstitial Cu or Ag atoms is known to be very high [1,2,3]. The influence of the respective lattice site on the diffusion of Ag or Cu in CdTe was discussed in an earlier work [4] and it was shown that Ag atoms are displaced by Cu atoms if both elements were diffused simultaneously into a CdTe crystal [4,5]. In this paper, the pronounced influence of intrinsic defects on the diffusion of Ag and Cu atoms is demonstrated and a model that describes the experimental diffusion profiles based on reactions between the group I elements and intrinsic defects of the Cd sublattice is presented.

Experimental details

The diffusion of Ag and Cu in CdTe was investigated following implantation of the radiotracers ¹¹¹Ag ($T_{1/2} = 7.5$ d) and ⁶⁷Cu ($T_{1/2} = 2.3$ d). For these experiments cylindrical crystals of 6 mm diameter and a thickness of either 0.5 mm or 0.8 mm were used. The crystals were polished on both sides from the supplier and were etched in a Br-methanol solution before implantation. The implantations were performed with an energy of 60 keV at the ISOLDE isotope separator (CERN, Geneva) or with 80 keV at the mass separator of the university of Bonn. After implantation, the Gaussian like Ag (Cu) profile is centered at a depth of about 30 (50) nm with a width of about 20 (30) nm. For diffusion annealing, performed at 700 K or 800 K, the crystals were enclosed in an evacuated quartz ampoule. The concentration-depth profile of intrinsic defects was altered by adding Cd or Te into the ampoule. For the determination of the concentration profiles, the crystals were mechanically polished and the γ -activity of the abraded layer was measured by a Ge well-detector. The thickness of the layer was determined by weighing of the polished crystal.

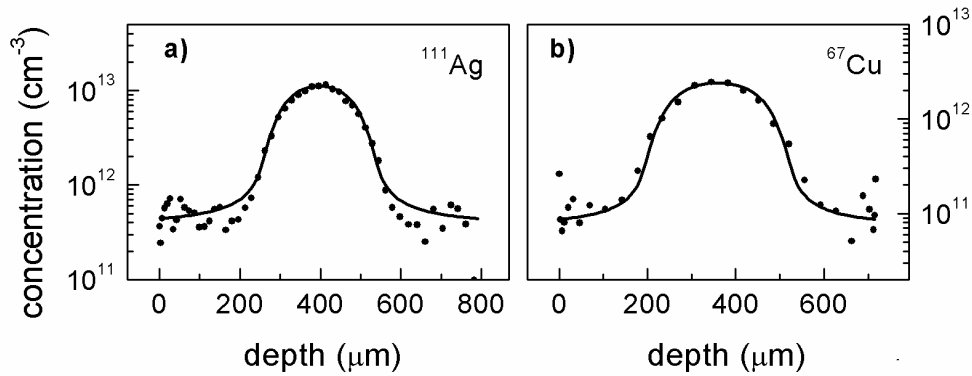


Fig. 1: Diffusion profiles after implantation of a) ^{111}Ag and b) ^{67}Cu into CdTe and subsequent annealing at 800 K for 60 min. The solid lines are the result of a simulation as discussed in the text.

Results

Fig. 1 shows concentration profiles after implantation of ^{111}Ag and ^{67}Cu with a dose of 10^{12} cm^{-2} and subsequent diffusion at 800 K (60 min) under Cd pressure. In both cases, the resulting quite unusual diffusion profiles exhibit a similar shape. Although the dopants were introduced from only one side to the crystal, the profiles are symmetric about the centre of the crystal, yielding the maximum concentration at the centre. From both surfaces strongly depleted layers extend over about $250\text{ }\mu\text{m}$ at a low constant concentration level. The shape of the profile changes drastically from peak shaped, like in Fig. 1, to U-shaped if the diffusion is performed under Te pressure [6]. Thus, the concentration profiles obtained in the diffusion experiments strongly depend on the external conditions used during the diffusion annealing. The development of the Ag profile as a function of diffusion time was investigated at a lower temperature of 700 K (Fig. 2). All profiles exhibit a pronounced step in the concentration starting from both sides of the implanted crystal. The position of the step as a function of the diffusion time, plotted in Fig. 3, shows up an almost \sqrt{t} dependence. After 15 min diffusion time the Ag profile is slightly asymmetric (Fig. 2a), while for longer diffusion times symmetric profiles are observed.

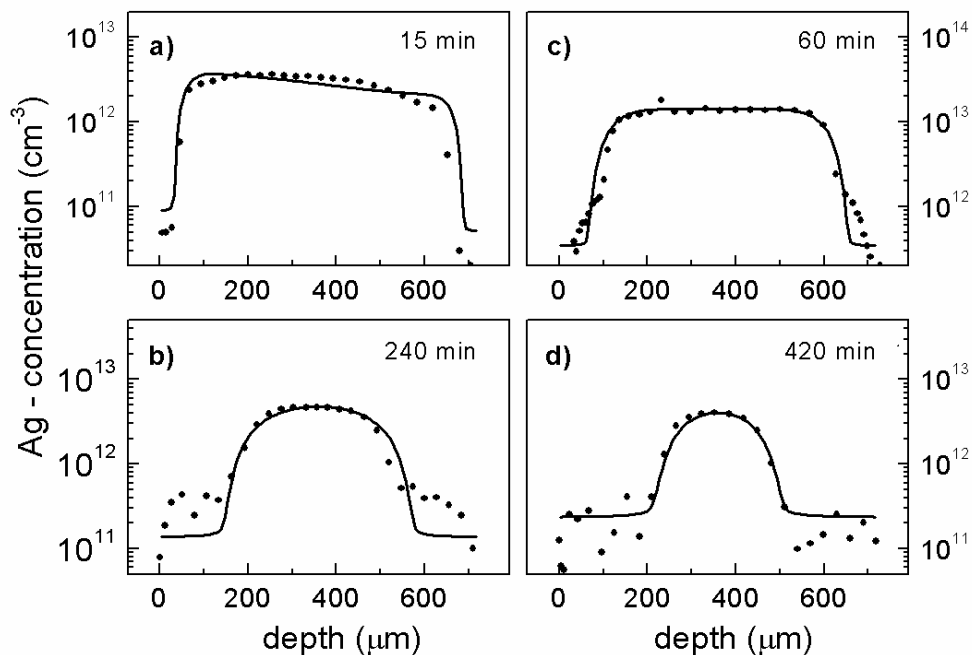


Fig. 2: Time dependent investigation of the diffusion of Ag in CdTe at 700 K. The solid lines correspond to simulations according to the model discussed in the text with a common set of parameters.

Discussion

The experimental data show that the diffusion profile of Ag can strongly be influenced by the external conditions during annealing. Since the external conditions, i.e. the presence of Cd or Te pressure, primarily affect the distribution of intrinsic defects, the diffusion profiles are obviously strongly determined by the diffusion and distribution of the intrinsic defects across the crystal. Thus, a model describing the experimental data has to include the diffusion of the intrinsic defects and the defect reactions between intrinsic defects and the dopant atoms. As the most simple model, outlined here for the case of Ag diffusion, only interstitial Cd atoms (Cd_i) and Cd vacancies (V_{Cd}) are considered as intrinsic defects and it is assumed that the dopant atoms are incorporated at interstitial sites (Ag_i) or on substitutional sites (Ag_{Cd}). The Te sublattice is treated as being perfect and should not change upon heat treatment. Thus, the profiles of the participating intrinsic (Cd_i , V_{Cd}) and extrinsic (Ag_i , Ag_{Cd}) defects as a function of diffusion time can be described by four coupled partial differential equations of the type

$$\left(\frac{d}{dt}\right)_{tot} [Y_j] = D(Y_j) \frac{d^2}{dx^2} [Y_j] - f([Y_1], [Y_2], [Y_3], [Y_4]), \quad (1)$$

where Y_j stands for Ag_i , Ag_{Cd} , Cd_i , and V_{Cd} , respectively and f is a non-linear function depending on all participating defects. The first term on the right hand side describes the concentration independent diffusion of the different defects according to Fick's laws and the second term takes into account the defect reactions



For the present analysis of the experimental data the model is treated in the limit of local equilibrium, i.e.:

$$[Ag_{Cd}] \cdot [Cd_i] = K_i \cdot [Ag_i] \cdot C_0, \quad (3a)$$

$$[Ag_i] \cdot [V_{Cd}] = K_s \cdot [Ag_{Cd}] \cdot C_0, \quad (3b)$$

$$[Cd_i] \cdot [V_{Cd}] = K_i \cdot K_s \cdot C_0^2 = \bar{C}^2, \quad (3c)$$

Here, Eq. (3c) follows directly from Eqs. (3a) and (3b) and $C_0 = 1.48 \cdot 10^{22} \text{ cm}^{-3}$ is the concentration of Cd-lattice sites. If all defects are normalized by \bar{C} , Eqs (3a) and (3b) become identical and the solutions of Eq. (1) depend only on the ratio K_s/K_i . In order to obtain absolute values of the different defect concentrations, additional information is needed yielding \bar{C} .

The Ag supply is treated as a layer deposited on the surface of the crystal. Defining the deviation from stoichiometry by

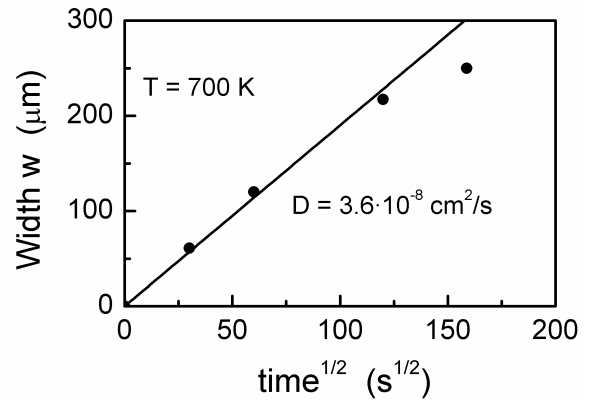


Fig. 3: Width w of the depletion layer as a function of diffusion time. The solid line correspond to a \sqrt{t} dependence.

$$\Delta C = [Cd_i] - [V_{Cd}], \quad (4)$$

the required initial and boundary conditions are related to the deviation from stoichiometry before diffusion (ΔC_i) and after diffusion in thermal equilibrium (ΔC_f) corresponding to the chosen external conditions, respectively. Besides the initial and boundary conditions, the model contains the four diffusion coefficients $D(Cd_i)$, $D(V_{Cd})$, $D(Ag_i)$, and $D(Ag_{Cd})$ as adjustable parameters along with the ratio of the equilibrium constants K_s/K_i . From thermodynamical properties of CdTe, the equilibrium concentrations of Cd_i and V_{Cd} as a function of temperature and external Cd pressure can be calculated as shown by Grill et al. [7] and Berding [8]. It turns out that \bar{C} besides on temperature depends on the deviation from stoichiometry ΔC . Thus, the normalization of the defect concentrations as described above is not exactly correct. Since the variation of \bar{C} in the range of ΔC values, accessible by thermal treatment under Cd or Te pressure, is only weak (see Table 1), the normalization of the defect concentrations still represents a good approximation for the present simulations.

The most noticeable features of the measured Ag (Cu) profiles are the depletion layer of width w , and the height h of the step-like increase of the concentration. In case of short diffusion times at low temperatures, additionally the slope s of the profile behind the step-like rise of the concentration is a characteristic feature, as is visible in Fig. 2a after 15 min diffusion time at 700 K. In case of $\Delta_f > \Delta_i$, like in case of diffusion under Cd pressure, and for $\sqrt{D(Cd_i) \cdot t_{diff}} > w$, these three characteristic features are controlled by the following three parameters

$$p = D(Cd_i) \cdot \sqrt{[Cd_i]_i / [V_{Cd}]_i}, \quad (5a)$$

$$q = D(Cd_i) \cdot \sqrt{K_i / K_s}, \text{ and} \quad (5b)$$

$$r = D(Ag_i) \cdot \sqrt{K_s \cdot [Cd_i]_i / K_i \cdot [V_{Cd}]_i} = D(Ag_i) \cdot p/q, \quad (5c)$$

where $[Cd_i]_i$ and $[V_{Cd}]_i$ are the initial concentrations of Cd_i and V_{Cd} . As shown in Fig. 4, the width w of the depletion layer is controlled by p according to $w \sim \sqrt{p \cdot t_{diff}}$ (Fig. 4b) and for $w = \text{const}$ the height h and the slope s by q and r , respectively (Fig. 4c, d). The slope of the step-like rise is significantly influenced by the diffusion coefficient $D(V_{Cd})$. Finally, as long as the maximum Ag concentration stays below the initial concentration of V_{Cd} , the shape of the simulated profile does not depend on the amount of Ag supplied for the diffusion experiment.

The experimental data are analyzed in the framework of the model discussed above in order to derive a consistent set of parameters. The parameters p , and q are directly determined from the width and height of the diffusion profiles with a good accuracy. For r , only a lower limit can be extracted in case of symmetric profiles. In case of an asymmetric profile, however, like in Fig. 2a, r can be also determined and, at the same time, the diffusion coefficient $D(Ag_i)$ is obtained via Eq. 5c. Since the parameters p and q each depend on three independent physical quantities and since a variation of $D(Cd_i)$, while keeping p and q constant, changes only slightly the curvature near the step-like increase of the profile, $D(Cd_i)$ can not be determined on the basis of the measured diffusion profiles alone. In addition, there might be other effects influencing the shape of the profile. Thus, the diffusion of the intrinsic defects through the outer mantle of the crystal and a finite tilt

temperature	external pressure	\bar{C} [cm^{-3}]	ΔC_f [cm^{-3}]
700 K	Cd	$7.9 \cdot 10^{13}$	$5.6 \cdot 10^{14}$
	Te	$14 \cdot 10^{13}$	$-160 \cdot 10^{14}$
800 K	Cd	$5.7 \cdot 10^{14}$	$2.5 \cdot 10^{15}$
	Te	$11 \cdot 10^{14}$	$-67 \cdot 10^{15}$

Table 1: Calculations of parameters related to the intrinsic defects according to thermodynamical parameters presented by Grill et al. [7] and Berding [8].

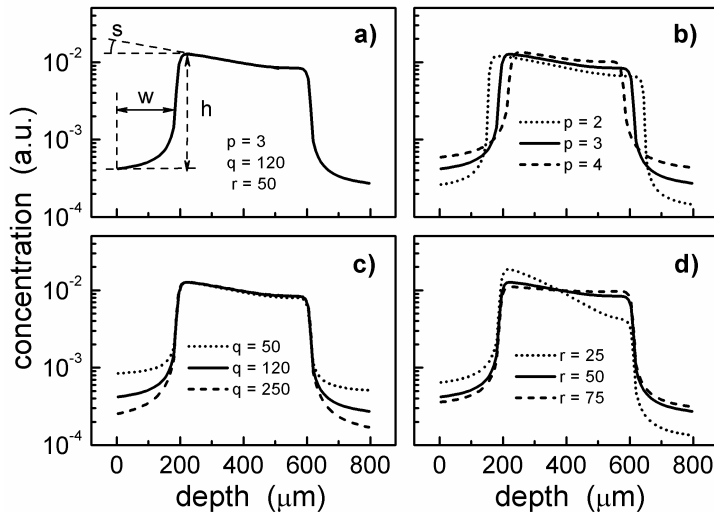


Fig. 4: Influence of the model parameters p , q , and r on the simulated dopant profiles. The different features width w , height h , and slope s (see Fig. 4a) can be altered almost independently by these parameters. All parameters are given in units of $10^{-8} \text{ cm}^2/\text{s}$.

angle during sectioning of the crystal can influence the sharpness of the the concentration step and the development of the adjacent curvature, as well. Consequently, additional information about the equilibrium constants or the initial deviation from stoichiometry ΔC_i is required in order to determine $D(\text{Cd}_i)$. Nonetheless, limits for $D(\text{Cd}_i)$ can be estimated: The lower limit is determined by the condition $\sqrt{D(\text{Cd}_i) \cdot t_{\text{diff}}} > w$. And, for the diffusion temperature of 800 K, the upper limit can be estimated on the basis of experimental observations made for Ag diffusion under Te pressure [6]. It turns out that the initial V_{Cd} concentration has to be lower than the equilibrium concentration of V_{Cd} upon thermal treatment under Te pressure at 800 K, which is calculated on the basis of the thermodynamical properties of CdTe [7,8] Then, the upper limit of $D(\text{Cd}_i)$ is calculated using Eq. 5a. Finally, the diffusion coefficient $D(V_{\text{Cd}})$ essentially affects the slope of the step-like rise. However, as mentioned above, there can be other reasons for smearing out the sharpness of the concentration step. Thus, only an upper limit for $D(V_{\text{Cd}})$ can be estimated.

The isothermal investigation of the Ag diffusion profiles at 700 K in Fig. 3 shows the propagation of the concentration step towards the centre of the crystal. Its position increases proportional to $\sqrt{t_{\text{diff}}}$ and, assuming a relation $w = \sqrt{D \cdot t_{\text{diff}}}$, a diffusion coefficient $D = 3.6 \cdot 10^{-8} \text{ cm}^2/\text{s}$ is obtained. A comparison with the chemical self diffusion coefficient of CdTe, which for 700 K is $D_{\text{SD}} = 4.3 \cdot 10^{-8} \text{ cm}^2/\text{s}$ according to Grill et al. [9], shows a good agreement with the value extracted from Fig. 3. The last data point at 420 min in Fig. 3 deviates from the proportionality to $\sqrt{t_{\text{diff}}}$ and seems to indicate that the propagation of the concentration step is slowed down when the diffusion fronts from both sides start to overlap. This retardation may be caused by the back-flow of the dopant atoms towards the surfaces of the crystal due to the filling up of the Cd vacancies in the centre of the crystal by the in-diffusing Cd interstitials. Also the simulations yield the relation $w \sim \sqrt{p \cdot t_{\text{diff}}}$ for the width of the depletion layer, indicating that the parameter p is closely connected to the chemical self diffusion coefficient. In fact, following a theoretical study by Guldi et al. for the case of PbS [10], in the present case of CdTe the proportionality $p \sim D_{\text{SD}}$ can be approximately expected to hold in the limit of high V_{Cd} concentrations.

The experimental data shown in Figs. 1 and 2 can now be fitted and it is assumed that the substitutional diffusion of Ag is negligible, i.e. $D(\text{Ag}_{\text{Cd}}) = 0$. The fits show that the diffusion coefficient $D(V_{\text{Cd}})$ must be much smaller than the diffusion coefficient $D(\text{Cd}_i)$. The parameters used for fitting the data measured after diffusion at 800 K (Fig. 1; Ag and Cu) and at 700 K (Fig. 2; Ag) are listed in Table 2; the results of the fits are shown by the solid lines in Figs. 1 and 2. The limits of $D(\text{Cd}_i)$ were determined as discussed above. Obviously, the present model already describes the different diffusion profiles very well. But, it should be noted that for describing the Cu and Ag profiles at 800 K different values for the width parameter p are needed, though this parameter should not depend on specific properties of the respective dopant. This may be an indication that the

Table 2: Model parameters used for fitting the data shown in Figs. 1 and 2. For all fits, the initial stoichiometry was set to $\Delta C_i = -10^{-16} \text{ cm}^{-3}$. The chemical self diffusion coefficient D_{SD} was calculated according to [9].

temperature	dopant Y	p [$\times 10^{-8} \text{ cm}^2/\text{s}$]	q [$\times 10^{-8} \text{ cm}^2/\text{s}$]	$D(Y_i)$ [$\times 10^{-8} \text{ cm}^2/\text{s}$]	$D(Cd_i)$ [$\times 10^{-8} \text{ cm}^2/\text{s}$]	$D(V_{Cd})$ [$\times 10^{-8} \text{ cm}^2/\text{s}$]	D_{SD} [$\times 10^{-8} \text{ cm}^2/\text{s}$]
700 K	Ag	0.2	8	4000	5 - 170	< 1	4.32
800 K	Ag	2.9	120	> 2000	25 - 350	< 5	44.0
	Cu	1.8	80	> 2000	15 - 220	< 5	

present model is not exact and more specific properties of the respective dopant atom have to be included. Nonetheless, the good agreement with the experimental data shows that the basic idea of the model is obviously correct and a quantitative agreement with experimental data for a larger variation of the external conditions may be attainable by some modifications.

Conclusions

A model based on defect reactions is presented describing the profiles observed after Ag or Cu diffusion. The model applies well in case of Ag (Cu) concentrations being below the initial concentration of Cd vacancies. The experimental data seem to be determined by the chemical self diffusion of CdTe since the diffusion coefficient extracted from the present data agrees well with data from literature. A more precise model should take into account the charge states of the different defects and include the chemical potential of the dopants instead of the more empirical reaction constants used here. In addition, other types of intrinsic defects, like defects on the Te sublattice and anti site atoms may be of importance for the final description of the measured diffusion profiles.

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