

Codoping Effects on the Diffusion of Ag in CdTe

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Abstract

The influence of Cu, Au and In on the diffusion of Ag in CdTe was investigated using the radiotracer ¹¹¹Ag. After evaporating a Cu layer on the ¹¹¹Ag implanted side of a CdTe single crystal and subsequent annealing at 550 K for 30 min most of the radioactive ¹¹¹Ag atoms was detected in a thin layer of only a few μm at the back of a 500 μm thick crystal. This behaviour is drastically different from the Ag diffusion without an evaporated Cu layer. The qualitatively identical effect is observed if a Au layer is used instead of a Cu-layer. But, the effect of pushing the Ag atoms to the back of the crystal takes place on a significantly longer time scale. In contrast, diffusing the Ag atoms into In doped CdTe results in a penetration of the Ag profile that is strongly retarded as compared to the diffusion of Ag into undoped CdTe.

Keywords: Diffusion, CdTe, Codiffusion, Group I element

1 Introduction

The group Ib elements Cu, Ag, and Au are important impurities in II-VI compound semiconductors since they represent potential acceptors. Besides the acceptor like incorporation on substitutional lattice sites, group Ib elements are reported to occupy interstitial lattice sites and to act as donor impurities. For Ag atoms a high diffusivity already at relatively low temperatures is reported [1,2,3]. The fact that the distribution of Ag and Cu in CdTe can be manipulated by varying the partial pressure of Cd or Te during diffusion and thereby changing the stoichiometry of the sample was shown in earlier work [4,5,6]. In this report, it will be shown that the diffusion of Ag is strongly influenced by the presence of an additional group I element, like Cu or Au, and the group III element In.

2 Experimental details

The diffusion of Ag was studied using the radiotracer ¹¹¹Ag which was implanted into CdTe single crystals. For these experiments, circularly

shaped crystals of 6 mm diameter and a thickness of about either 0.5 mm or 0.8 mm were used. The crystals were received polished on both sides from the supplier and were etched in bromine methanol solution before implantation. The implantations were performed with energy of 60 keV at the ISOLDE isotope separator (CERN, Geneva) or with 80 keV at the mass separator of the university of Bonn. Under these conditions the Gaussian like Ag profile is located at a depth of about 30 nm. For the codiffusion experiments, a layer of Cu or Au was evaporated onto the implanted side of the crystal. For diffusion annealing, performed at temperatures between 550 K and 800 K for different times, the crystal was enclosed in an evacuated quartz ampoule. In order to provide a partial pressure of Cd, few mg of Cd metal were added into the quartz ampoule. The concentration profile of ¹¹¹Ag was determined by mechanical polishing of the crystal and measuring of the γ -activity of the abraded layer using a Ge well-detector. The thickness of the abraded layer was determined by weighing of the polished crystal.

3 Results

Ag Diffusion under Cd pressure

The diffusion of Ag into CdTe under Cd or Te pressure was investigated in earlier work [4,5,6]. It was observed that the diffusion of ^{111}Ag under Cd pressure at 800 K for 60 min into an 800 μm thick crystal leads to a symmetrical, peak shaped concentration profile at the centre of the crystal followed by depletion layers of about 300 μm towards both surfaces (Fig. 1). The experimental data are well described in the framework of a model based on reactions of the dopant atom Ag with intrinsic defects of the Cd sublattice, i.e. Cd interstitials (Cd_i) and Cd vacancies (V_{Cd}). The solid line in Fig. 1 shows a simulation of the corresponding Ag profile based on this defect reaction model. In addition, the corresponding distribution of the intrinsic defects represented by the ratio of the concentrations $[\text{Cd}_i]/[\text{V}_{\text{Cd}}]$ is plotted (dashed line). The CdTe crystals as delivered are expected to be Te rich. Thus, the Cd pressure applied changes the distribution of the intrinsic defects due to chemical self diffusion what is reflected by the increased ratio $[\text{Cd}_i]/[\text{V}_{\text{Cd}}]$ towards both surfaces of the sample. Obviously, the ^{111}Ag profile essentially reflects the actual distribution of the intrinsic defects.

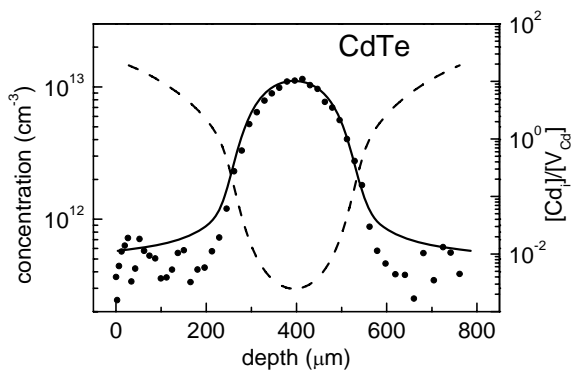


Figure 1: Ag profile in CdTe after diffusion at 800 K for 60 min under Cd pressure. The solid line shows a simulation of the Ag profile and the dashed line the corresponding ratio of intrinsic defects $[\text{Cd}_i]/[\text{V}_{\text{Cd}}]$.

Codiffusion of Cu.

Diffusing Ag into CdTe at 570 K for 30 min under vacuum leads to a monotonously decreasing concentration profile appears and the penetration depth reaches less than 100 μm (open circles in

Fig. 2). Whereas such a profile is expected in case of a common diffusion process, the shape of the profile drastically changes if a Cu layers was evaporated onto the implanted side of the crystal before diffusion [6]. After diffusion at 550 K for 30 min under vacuum, the Ag atoms are nearly completely pushed into a thin layer of only few μm at the back of the crystal, while in the interior of the sample the Ag concentration significantly dropped below 10^{12} cm^{-3} (closed circles in Fig. 2).

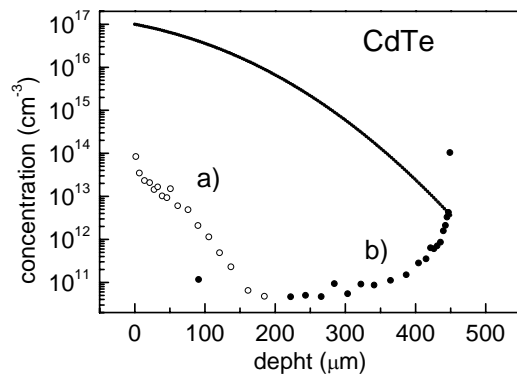


Figure 2: Ag profiles after a) diffusion at 570 K for 30 min and b) 550 K for 30 min obtained upon codiffusion of Cu. The solid line shows the calculated diffusion profile according to Jones et al. [7].

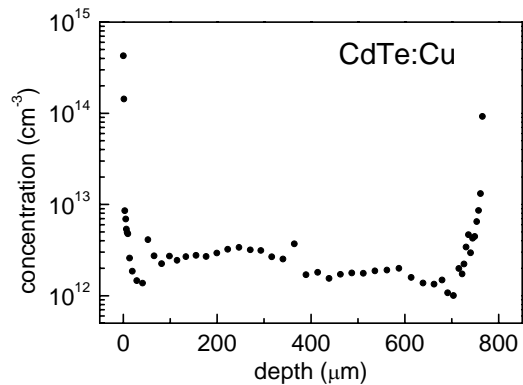


Figure 3: Ag profile after diffusion at 550 K for 30 min in Cu doped CdTe

The influence of Cu on the diffusion of Ag in CdTe was also investigated in a sample previously doped with Cu. For this purpose, a Cu layer of 30 nm thickness was evaporated onto one side of a CdTe crystal and subsequently heated at 800 K for 2 h under vacuum. After this pre-treatment ^{111}Ag atoms were implanted into the crystal. The Ag profile obtained after diffusion at 550 K for 30 min is shown in Fig. 3. Now, a homogeneous

Ag profile at a concentration of about $3 \cdot 10^{12} \text{ cm}^{-3}$ is present and the excess Ag is segregated at the surfaces of the crystal. Both experiments in figs. 2 and 3 illustrate that the presence of Cu drastically enhance the diffusion and affects the solubility of Ag in CdTe.

Codiffusion of Au.

Beside the codiffusion of Ag and Cu also the codiffusion of Ag and Au was investigated. In this case, a 30 nm Au layer was evaporated onto the ^{111}Ag implanted side of a CdTe crystal. The ^{111}Ag profiles obtained after diffusion at 550 K for 30 min and 120 min are shown in Fig 4. In contrast to the codiffusion experiment with Cu (closed circles in Fig. 2), now the Ag atoms are not completely pushed to the backside of the crystal but a depletion layer emerges from the Au evaporated side of the crystal. This depletion layer increases with diffusion time extending about 200 μm after 30 min and about 400 μm after 120 min. In case of 30 min diffusion time, the decrease of the Ag profile at depths larger than 200 μm reflects the diffusion range of Ag under these conditions and does not correspond to a depletion layer as observed at smaller depth at the front side of the sample.

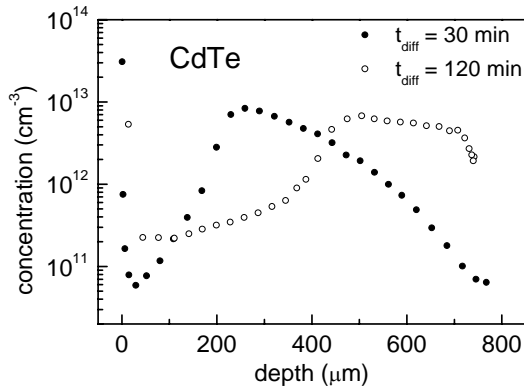


Figure 4: Ag profiles after diffusion at 550 K obtained upon codiffusion of Au for different diffusion times.

Ag diffusion in CdTe:In

Diffusing Ag into a CdTe crystal homogeneously doped with In donors results in drastically different diffusion profiles as it is shown in Fig. 5. Inspecting the Ag-profiles obtained after diffusion at 800 K for 240 min under vacuum (open circles) and under Cd

pressure (closed circles) it is evident that the diffusion of Ag is significantly retarded in the In doped material. In particular, the penetration depth of Ag under Cd pressure is only about 300 μm and, therefore, significantly smaller compared to the undoped material shown in fig. 1. In contrast to undoped CdTe also the influence of the external vapour pressure seems to be weak since only a weak depletion layer emerged (closed circles).

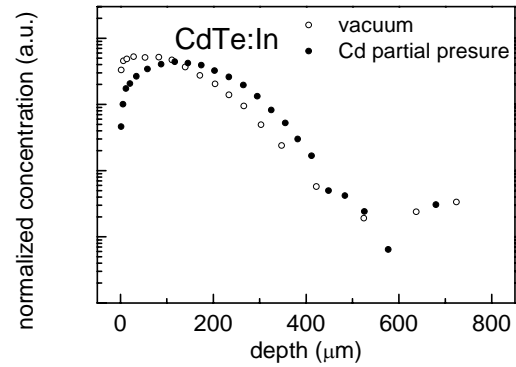
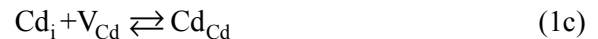


Figure 5: Ag profile after diffusion at 800 K for 240 min in In doped CdTe under vacuum (open circles) and Cd pressure (closed circles). The profiles are normalized to the respective maximum concentration.

4 Discussion

The unusual shape of the Ag profiles, as observed e.g. after diffusion at 800 K for 60 min under Cd pressure (see Fig. 1), has been discussed in earlier publications [4,5] and is well understood in terms of the interaction of Ag dopant atoms with intrinsic defects of the Cd sublattice:

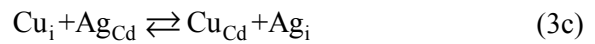


Assuming local thermal equilibrium, these reactions lead to a relation that connects the concentrations of the extrinsic and the intrinsic defects:

$$\sqrt{\frac{[\text{Cd}_i]}{[\text{V}_{\text{Cd}}]}} = k_{\text{Ag}} \cdot \frac{[\text{Ag}_i]}{[\text{Ag}_{\text{Cd}}]} \quad (2)$$

Here, k_{Ag} is a temperature dependent equilibrium constant which determines the fraction of substitutionally incorporated Ag atoms. In addition, the model makes the following assumptions: (i) Ag diffuses exclusively interstitially. (ii) The diffusion coefficient $D(Ag_i)$ of the Ag_i defects is larger than the diffusion coefficient $D(Cd_i)$ of Cd_i defects. (iii) The diffusion coefficient $D(V_{Cd})$ of Cd vacancies is much smaller than $D(Cd_i)$. For describing the profile shown in Fig. 1 it is required that the deviation from stoichiometry $\Delta C = [Cd_i] - [V_{Cd}]$ during the diffusion process varies over a sufficiently large range from negative (Te-rich material) to positive (Cd-rich material) values. The dashed line in Fig. 1 shows the ratio $[Cd_i]/[V_{Cd}]$, which is a measure of the deviation from stoichiometry since the product $[Cd_i] \cdot [V_{Cd}]$ is a constant depending only on temperature. According to Eq. (2) the concentration of Ag_{Cd} atoms decreases in favour of Ag_i atoms if the Cd_i concentration is increased. Thus, the depletion layers in the Ag profile of Fig. 1 correspond to regions with an increased ratio $[Cd_i]/[V_{Cd}]$, caused by Cd_i atoms that are created by the Cd partial pressure according to reaction 1c. Most of the Ag atoms in this layer are incorporated at interstitial lattice sites, diffuse rapidly as Ag_i atoms into the V_{Cd} -rich center of the sample and are incorporated on Cd lattice sites according to reaction 1b. Consequently, the Ag distribution is determined by the concentration of the Ag_{Cd} atoms and directly reflects the stoichiometry of the sample after the corresponding diffusion process.

The Ag profile obtained after codiffusion of Cu at 550 K for 30 min (Fig. 2b) shows that the Ag atoms were pushed to the back of the crystal. Obviously the Ag diffusion is strongly enhanced upon codiffusion of Cu compared to Ag diffusion without codoping (Fig. 2a). By comparing the Ag profile, obtained after codiffusion of Cu, with the Cu profile as expected on the basis of the fast diffusing component reported in ref. [7] it turns out that the Ag profile exhibits an inverted behaviour as compared to the Cu profile (solid line in Fig. 2). It is suggested that there exists a seemingly repulsive interaction between Ag and Cu atoms in CdTe. In order to describe the codiffusion of Ag and Cu the following defect reactions have to be added to reactions 1a-1c:



The first two reactions describe the interaction of Cu atoms with the intrinsic defects of the Cd sublattice and are equivalent to the reactions (1a) and (1b); reaction (3c) describes the mutual interaction between Ag and Cu atoms. The corresponding local equilibrium conditions yield

$$\sqrt{\frac{[Cd_i]}{[V_{Cd}]}} = k_{Ag} \cdot \frac{[Ag_i]}{[Ag_{Cd}]} = k_{Cu} \cdot \frac{[Cu_i]}{[Cu_{Cd}]} \quad (4)$$

where k_{Cu} is, like k_{Ag} , a temperature dependent equilibrium constant. Assuming that Cu like Ag diffuses exclusively interstitially, according to Eq. 4 the codiffusion of Cu_i atoms leads to a change of the distribution of intrinsic defects and thereby to a decrease of the concentration of Ag_{Cd} atoms in favour of Ag_i atoms. As a consequence, the highly mobile Ag_i defects will diffuse into regions with higher V_{Cd} concentrations, i.e. towards the back of the crystal where the Cu concentration is still low, and, according to reaction 1b, they will be incorporated as immobile substitutional Ag_{Cd} defects.

The data obtained after Ag diffusion into a CdTe crystal pre-doped with Cu show that in this case Ag is incorporated only at a low concentration level and the excess of Ag atoms segregates at the surfaces (Fig. 3). Since the pre-doping was performed using a 30 nm Cu layer followed by annealing at 800 K for 120 min a homogeneous Cu concentration of about $4 \cdot 10^{18} \text{ cm}^{-3}$ is estimated, which was also verified by an independent diffusion measurement using ^{67}Cu . According to reaction (3b), in this pre-doped crystal a low V_{Cd} concentration is expected to be present if Cu diffuses interstitially into CdTe and, therefore, only a small part of the in-diffusing Ag atoms can be incorporated on substitutional lattice sites. The segregation of Ag atoms at the surfaces becomes understandable if the surface of CdTe acts as a drain for the highly mobile interstitial Ag_i atoms. At present, however, no decision can be made, whether the excess Ag at the surface resides as metal precipitates or has formed a new phase like e.g. Ag_2Te .

The codiffusion of Au shows a depletion layer of the Ag profile, which increases from 200 μm to

400 μm if the diffusion time is increased from 30 min to 120 min (Fig. 4). Obviously there is an apparent repulsive interaction present between Ag and Au atoms, too. But the interaction is significantly weaker than in case of Cu. The width of the depletion layer seems to follow a \sqrt{t} -dependence, suggesting that it is correlated with the diffusion length of Au. Assuming that the width Δx of the depletion layer agrees with the diffusion length of Au, i.e.

$$\Delta x = \sqrt{D(\text{Au}) \cdot t}, \quad (5)$$

a diffusion coefficient of $D(\text{Au}) \approx 2 \cdot 10^{-7} \text{ cm}^2/\text{s}$ for Au at 550 K is obtained. However, this value is in strong contrast to values available in the literature. Interpolating the diffusion coefficient $D(\text{Au})$ from Hage-Ali et al. [8], $D(\text{Au}) \approx 2.4 \cdot 10^{-18} \text{ cm}^2/\text{s}$ is obtained and extrapolating the data from Teramoto et al. [9] yields $D(\text{Au}) \approx 3.2 \cdot 10^{-18} \text{ cm}^2/\text{s}$; both values being far off the estimate given above. An explanation might be found in the presence of a second, fast diffusion component like in case of Cu, which was not reported by Hage-Ali and Teramoto. Such an assumption might be supported by the presence of a fast diffusing component reported for Au in $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ [10]. Diffusing Ag into In doped CdTe a completely different behaviour is observed. The Ag profile obtained at a diffusion temperature of 800 K for 240 min under vacuum is shown by the open circles in Fig. 5. Performing the same diffusion experiment under Cd pressure the range of the Ag profile extends by about 50 μm further and a weak depletion layer of about 70 μm emerges at the surface (closed circles). In contrast, the profile in Fig. 1 obtained at the same temperature under Cd pressure but for a much shorter time of 60 min in an undoped CdTe crystal shows the symmetric peak shaped Ag profile accompanied by much stronger depletion layers of about 300 μm at both surfaces. Obviously the diffusion of Ag is strongly retarded in In doped CdTe compared to undoped material. A similar observation was made by Lyubomirsky et al., who have investigated the diffusion of Ag in In doped CdTe at 473 K [11]. In this experiment the penetration of Ag reached only about 25 μm after 8 h diffusion time. An explanation might be found in terms of self compensation, i.e. the compensation of the In_{Cd} donors by V_{Cd} defects acting as double acceptors.

In case of full compensation the additional concentration of Cd vacancies, which partially might be present as A-centres ($\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pairs), essentially agrees with half of the In concentration, being about 10^{17} cm^{-3} in the present case. The V_{Cd} concentration, including A-centres, therefore, might be significantly larger than in the investigated undoped crystals where the V_{Cd} concentration was determined by the initial deviation from stoichiometry. Consequently, compared to undoped material, from the indiffusing Ag atoms a larger fraction might be incorporated substitutionally being no longer mobile. In addition, Ag atoms that occupy Cd vacancies bound in A-centres will form close donor acceptor pairs $\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$, which might be still more stable than isolated Ag_{Cd} defects. As a consequence, the equilibrium concentration of mobile Ag_i defects is reduced in favour of Ag_{Cd} atoms, thereby, retarding the diffusion of the Ag atoms. The higher stability of $\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$ pairs might also explain the less pronounced depletion layer since in this case only a smaller fraction of Ag atoms will be moved to interstitial lattice sites by the incorporated Cd_i defects.

5 Summary

The diffusion of Ag in CdTe is strongly influenced by the presence of other impurities. It has been shown that the diffusion of Ag is strongly enhanced upon codiffusion of Cu or Au. At the same time the Ag atoms are driven out of regions of high concentrations of Cu or Au atoms. The enhanced Ag diffusion is more pronounced in case of codiffusion of Cu than of Au. It is concluded that this effect is essentially governed by the diffusion coefficients of Cu and Au. The present data are explained in terms of a replacement of substitutionally incorporated Ag atoms by Cu or Au atoms. In contrast, Ag diffusion is remarkably retarded in In doped CdTe. It is proposed that a higher V_{Cd} concentration exists as compared to undoped material due to self compensation of the In donors. In addition, a higher stability of Ag atoms bound in $\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$ pairs is responsible for this retardation effect.

Acknowledgments

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