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# The unusual influence of intrinsic defects on the diffusion of Ag and Cu in CdTe

H. Wolf<sup>a,\*</sup>, F. Wagner<sup>a</sup>, T. Wichert<sup>a</sup>, ISOLDE collaboration<sup>b</sup>

<sup>a</sup> *Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany*

<sup>b</sup> *CERN, EP Division, CH-1211 Geneva 23, Switzerland*

## Abstract

The diffusion of Ag and Cu in CdTe was investigated using the radiotracers <sup>111</sup>Ag and <sup>67</sup>Cu. The diffusion properties are similar for both dopants and are essentially determined by diffusion of intrinsic defects in the crystal. Both dopants show up interstitial fractions which are incorporated substitutionally if Cd vacancies are present. The resulting unusual diffusion profiles map the actual distribution of the intrinsic defects and indicate the chemical self diffusion in CdTe. © 2003 Elsevier B.V. All rights reserved.

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## 1. 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 that can be 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 also as interstitial donors and the mobility of interstitial Cu or Ag atoms is known to be very high [1–3]. The diffusion of Ag or Cu in CdTe, therefore, seems

to depend strongly on the occupied lattice sites. In this report, the pronounced influence of intrinsic defects on the diffusion of Ag and Cu atoms is demonstrated.

## 2. Experimental details

The diffusion of Ag and Cu in CdTe was investigated using the implanted radiotracers <sup>111</sup>Ag ( $T_{1/2} = 7.5$  d) and <sup>67</sup>Cu ( $T_{1/2} = 2.3$  d). For the experiments circularly shaped crystal of 6 mm diameter and a thickness of about either 0.5 or 0.8 mm were used. The crystals were polished on both sides from the supplier and 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

\*Corresponding author. Physik und Elektrotechnik, Universität des Saarlandes, P.O. Box 151150, D-66041 Saarbrücken, Germany. Tel.: +49-681-302-2038; fax: +46-681-302-4315.

E-mail address: [h.wolf@mx.uni-saarland.de](mailto:h.wolf@mx.uni-saarland.de) (H. Wolf).

the University of Bonn. After implantation, the Gaussian-like Ag (Cu) profile is centred at a depth of about 30 (50) nm with a width of about 20 (30) nm. For diffusion annealing, performed at temperatures between 550 and 800 K for 30 or 60 min, the crystals were enclosed in an evacuated quartz ampoule. The distribution of intrinsic defects was modified by adding Cd or Te into the ampoule used for the diffusion process. For the determination of the concentration profiles, the crystals were mechanically polished and the  $\gamma$  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.

### 3. Results

The  $^{111}\text{Ag}$  profile obtained after diffusion at 800 K for 60 min is plotted in Fig. 1a. The diffusion was performed under Cd pressure at a temperature of 800 K. The resulting peak shaped profile is symmetrical about the centre of the

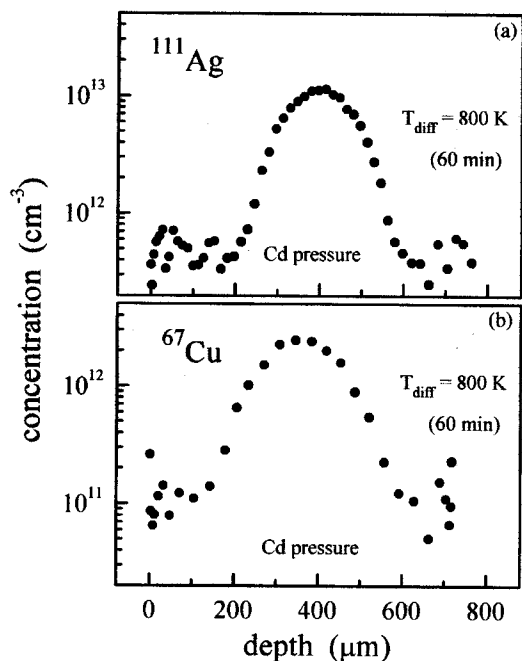


Fig. 1. Diffusion profiles of (a)  $^{111}\text{Ag}$  and (b)  $^{67}\text{Cu}$  in CdTe after diffusion at 800 K for 60 min under external Cd pressure. The original implantation profile was  $\delta$ -like at  $x = 0$ .

crystal and exhibits a strongly depleted region of about 250  $\mu\text{m}$  towards both surfaces of the 800  $\mu\text{m}$  thick crystal. In contrast, diffusion under Te pressure causes a layer of about 20  $\mu\text{m}$  below the surface containing a high concentration of Ag atoms, whereas the Ag concentration in the interior of the crystal is strongly depleted and slightly decreases towards the back side of the crystal. For comparison, the profile observed after diffusion under vacuum [4] is almost symmetrical and exhibits a nearly constant Ag concentration profile in the interior of the crystal followed by depletion layers of about 100  $\mu\text{m}$  towards both surfaces.

Besides the diffusion of Ag, the diffusion of  $^{67}\text{Cu}$  was investigated upon annealing under Cd pressure at 800 K (60 min). The observed Cu profile (Fig. 1b) exhibits a very similar shape compared to that obtained after Ag diffusion under the same conditions (see Fig. 1a). In earlier investigations a strong repulsive interaction between Ag and Cu was reported after evaporation of a Cu layer onto the surface of a  $^{111}\text{Ag}$ -implanted CdTe crystal and subsequent diffusion at 550 K for 30 min [4]. As a consequence, the  $^{111}\text{Ag}$  atoms were nearly completely pushed to the back side of the implanted crystal (Fig. 2a). In that experiment much more Cu than Ag was supplied for the diffusion process and it remained an open question whether implanted Cu would also be pushed through the crystal by Ag atoms that are provided by an evaporated Ag layer. Fig. 2b shows the  $^{67}\text{Cu}$  profile measured after implantation of  $^{67}\text{Cu}$  and subsequent evaporation of 30 nm Ag onto the implanted surface of the crystal. The diffusion annealing was performed under identical conditions (550 K for 30 min) used for the  $^{111}\text{Ag}$  experiment displayed in Fig. 2a. It is obvious that in this case the  $^{67}\text{Cu}$  atoms are not pushed to the back side of the crystal upon co-diffusion of Ag atoms.

### 4. Discussion

The data obtained after diffusion at 800 K for 60 min show that the  $^{111}\text{Ag}$  profile drastically depends on the external partial pressures of Cd and Te. Fig. 1a shows the case of Ag diffusion under

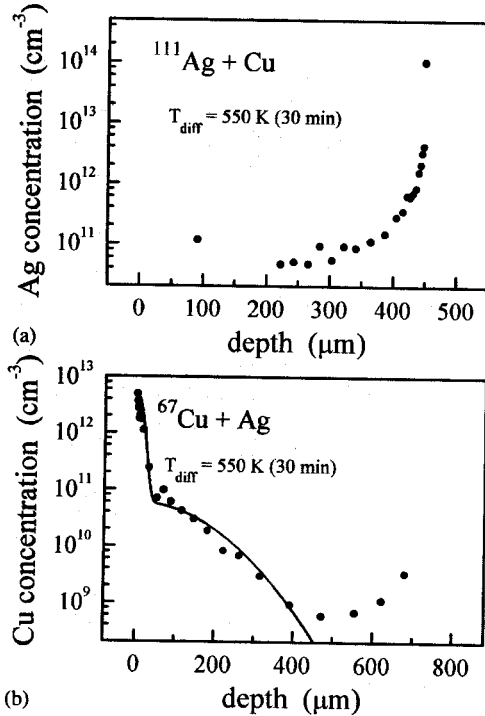


Fig. 2. Concentration profiles observed after co-diffusion of Ag and Cu: (a)  $^{111}\text{Ag}$  profile upon co-diffusion with Cu and (b)  $^{67}\text{Cu}$  profile upon co-diffusion with Ag.

Cd atmosphere. Obviously, the respective external partial pressure alters the stoichiometry of the crystal. Assuming that the Te sublattice is perfect and not affected by the different thermal treatments in a significant way, the stoichiometry of the crystal is controlled by the presence of Cd interstitials ( $\text{Cd}_i$ ) and Cd vacancies ( $\text{V}_{\text{Cd}}$ ). Consequently, annealing under Cd pressure will reduce, and annealing under Te pressure will increase the concentration of  $\text{V}_{\text{Cd}}$ . In addition, assuming that Ag is only incorporated either substitutionally ( $\text{Ag}_s$ ) or interstitially ( $\text{Ag}_i$ ), i.e. the potential formation of complexes containing more than one Ag atom is neglected, the incorporation of Ag in CdTe is determined by the following defect reactions:



And, the corresponding thermal equilibrium conditions are described by

$$[\text{Ag}_s][\text{Cd}_i] = K_i [\text{Ag}_i] C_0, \quad (2a)$$

$$[\text{Ag}_i][\text{V}_{\text{Cd}}] = K_s [\text{Ag}_s] C_0, \quad (2b)$$

$$[\text{Cd}_i][\text{V}_{\text{Cd}}] = K_0 C_0^2, \quad (2c)$$

whereby the temperature-dependent equilibrium constants  $K_i$ ,  $K_s$  and  $K_0 = K_i K_s$  are independent of the respective defect concentrations. Using Eqs. (2a) and (2b), the ratio of the concentrations of interstitially and substitutionally incorporated Ag can be expressed with help of the ratio of the concentrations of the intrinsic defects yielding

$$\frac{[\text{Ag}_i]}{[\text{Ag}_s]} = \sqrt{\frac{K_s}{K_i}} \sqrt{\frac{[\text{Cd}_i]}{[\text{V}_{\text{Cd}}]}} \quad (3)$$

From Eq. (3) it is obvious that the concentration of  $\text{Ag}_s$  atoms decreases in favour of  $\text{Ag}_i$  atoms if the concentration of Cd interstitials is increased.

A consistent explanation of the experimental diffusion profiles is obtained if it is assumed that interstitially incorporated Ag atoms are highly mobile in agreement with reports in the literature [2], and that the mobility of substitutionally incorporated Ag can be neglected. Using this model and taking into account that the diffusion profile corresponds to  $\text{Ag}_s$  atoms, the depletion layers observed in Fig. 1a correspond to regions of the crystal where the ratio  $[\text{Cd}_i]/[\text{V}_{\text{Cd}}]$  is high, which can be expected due to the thermal treatment under Cd vapour. Because of their high mobility the interstitially incorporated Ag atoms quickly diffuse into a region of a higher  $\text{V}_{\text{Cd}}$  concentration, which seems to be present in the inner part of the crystal. There, the  $\text{Ag}_i$  atoms are converted into  $\text{Ag}_s$  atoms according to Eq. (1b) and are no longer mobile. The height of the concentration peak with respect to the concentration in the depletion layers is determined by the ratio  $K_s/K_i$  of the equilibrium constants and the change of the ratio of the concentrations of the intrinsic defects  $[\text{Cd}_i]/[\text{V}_{\text{Cd}}]$  during the diffusion process. The required low stability of  $\text{Ag}_s$  atoms is equivalent to a large ratio  $K_s/K_i$ . In addition,  $[\text{Cd}_i]/[\text{V}_{\text{Cd}}]$  has to change sufficiently by

the diffusion annealing under Cd atmosphere. Since the ratio  $[Cd_i]/[V_{Cd}]$  directly corresponds to the deviation from stoichiometry, the Ag profile reflects the stoichiometric conditions of the crystal as a function of depth. The initial condition of the sample, therefore, has to correspond to a Te-rich CdTe crystal that is converted into a Cd-rich crystal during the diffusion process. The very pronounced shape of the profile is caused by the strong variation of the stoichiometry of the crystal upon the thermal treatment under Cd atmosphere. The range of the wing of the Ag profile indicates the range of the  $Cd_i$  atoms penetrated into the CdTe crystal. The observed Ag profile, therefore, should directly reflect the distribution of intrinsic defects as outlined by Zimmermann et al. [5]. Consequently, the diffusion profiles of Ag should be the result of the so-called chemical self diffusion in CdTe, which describes the variation of the stoichiometry as a function of depth and time due to annealing under the respective external vapour pressures of Cd and Te. Using the chemical self-diffusion coefficient reported by Grill et al. [6]

$$D_{SD} = 5 \exp(-1.12 \text{ eV}/k_B T) \text{ cm}^2/\text{s}, \quad (4)$$

$D_{SD}$  is calculated to  $4.4 \times 10^{-7} \text{ cm}^2/\text{s}$  at 800 K, yielding a diffusion length of 400  $\mu\text{m}$ . This value is in good agreement with the width of the depletion layers of the Ag profile shown in Fig. 1a.

In contrast, after diffusion of Ag under Te pressure about 50% of the Ag atoms remained within a layer of about 20  $\mu\text{m}$  below the implanted CdTe surface. Since the  $V_{Cd}$  concentration near the surface is increased by this treatment and the existing Cd vacancies are not annihilated by interstitial Cd atoms, a much higher fraction of Ag was incorporated as substitutional atoms being much less mobile. Only the remaining part of the Ag atoms diffuses as interstitials until Cd vacancies in the interior of the crystal are reached and occupied according to Eq. (1b). As a consequence, the current of  $Ag_i$  atoms towards the interior of the sample is depleted which explains the slight decrease in the concentration profile, mentioned before.

Finally, the Ag profile observed at a 500  $\mu\text{m}$  thick crystal after diffusion under vacuum as reported in Ref. [4] shows less-pronounced depletion zones below both surfaces if compared with the diffusion under Cd pressure. The equilibrium concentration of Cd vacancies and consequently that of  $Ag_s$  atoms, corresponding to a diffusion temperature of 800 K, is obviously lower than in the CdTe sample after crystal growth ( $d = 800 \mu\text{m}$ , see Fig. 1a). Since there is no external Cd pressure supplied, the adjustment of the distribution of intrinsic defects is not caused by the in-diffusion of Cd interstitials but by the out-diffusion of Cd vacancies.

With regard to the diffusion of Cu in CdTe the following information is obtained: (i) The shape of the Cu profile shown in Fig. 1b after diffusion at 800 K under Cd pressure is very similar to that obtained in case of Ag under the same experimental conditions. This comparison indicates that the diffusion properties of both group I elements, Cu and Ag, seem to be quite similar. (ii) The fast diffusing interstitial Cu atoms can be compared with the fast diffusing component of Cu atoms published by Jones et al. [7]. Its diffusion coefficient, measured in the range between 500 and 700 K, is in the order of  $10^{-7} \text{ cm}^2/\text{s}$  but does not vary systematically with temperature. With regard to the data in Fig. 1b, this diffusivity is consistent with a distribution of  $Cu_i$  atoms across the whole crystal at a diffusion temperature of 800 K. In general, also for Cu a low stability on substitutional Cd site is required in order to explain the diffusion profile displayed in Fig. 1b. With regard to the data in Fig. 2b it is obvious that  $^{67}\text{Cu}$  is not pushed to the back side of the crystal upon co-diffusion of Ag. Therefore, the stability of Cu on substitutional sites has to be higher than the stability of substitutional Ag atoms. The experimental  $^{67}\text{Cu}$  profile is well described using the diffusion coefficients reported by Jones et al., and assuming Gaussian profiles with a surface concentration of  $5 \times 10^{12} \text{ cm}^{-3}$  for the slow and of  $6 \times 10^{10} \text{ cm}^{-3}$  for the fast diffusing component (solid line in Fig. 2b). Possibly, a slight increase in the Cu concentration at depths larger than 500  $\mu\text{m}$  might indicate that also a weak replacement effect by the Ag atoms does exist.

## 5. Conclusion/future work

The diffusion properties of Ag and Cu in CdTe are strongly determined by the diffusion of the intrinsic defects  $Cd_i$  and  $V_{Cd}$ . The initial distribution of intrinsic defects can significantly be changed by a thermal treatment under distinct partial pressures of Cd or Te. The Ag profile obtained after a sufficiently long diffusion time directly reflects the distribution of intrinsic defects. Based on a quantitative analysis of the experimental diffusion profiles, it should be possible to determine the ratio of the concentrations of both types of intrinsic defects  $[Cd_i]/[V_{Cd}]$  and the ratio of the equilibrium constants  $K_s/K_i$ . In addition, by measuring the development of the diffusion profiles of group I elements as a function of time a determination of the diffusion coefficients of the four participating defects should become possible. It might be necessary, however, to take into account also the charge states of the different defects which might change the diffusion properties of the participating defects.

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