

The Strange Diffusivity of Ag Atoms in CdTe

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Abstract

The diffusion of Ag atoms in CdTe was investigated using the radiotracer ^{111}Ag , which was introduced by implantation with an energy of 60 or 80 keV. The measured diffusion profiles are explained by assuming the existence of a repulsive interaction between Ag and residual Cu atoms causing a drift of the Ag atoms towards the centre of the crystal, which supposes the diffusion in a concentration gradient. This effect vanishes if the Ag concentration is increased and becomes more pronounced if the crystals are simultaneously co-doped with Cu.

Keywords: Ag, Cu, diffusion, CdTe

Introduction

The electrical and optical properties of semiconductors are essentially determined by the presence of impurities and defects. In addition, for the construction and thermal stability of devices, dynamic properties of dopant atoms are important. In CdTe, the group I elements represent potential acceptor atoms if they are incorporated substitutionally on Cd sites. The hole concentration achieved upon doping of CdTe with Ag atoms, however, is limited to about 10^{16} cm^{-3} , although much higher concentrations of Ag are realised [1]. The formation of compensating defect complexes strongly depends on the concentration and the mobility of the participating defects. For Ag atoms in CdTe, the mobility is known to be very high, the the experimental data describing the diffusion of Ag in CdTe in the literature are difficult to compare [2,3,4,5].

Experimental details

^{111}Ag atoms were implanted into CdTe single crystals using either the mass separator at the university Bonn or the isotope separator ISOLDE at CERN. The energy and dose used for implantation of the different samples are listed in Table 1. In order to investigate the influence of a higher Ag concentration, a 30 nm thick layer of stable Ag was deposited onto a CdTe crystal and the ^{111}Ag atoms were implanted into this layer. In addition, the influence of Cu on the diffusion of Ag was investigated. For this purpose, a 20 nm thick Cu layer was deposited onto the side implanted with ^{111}Ag (sample #5) before annealing of the crystal. In each case, the diffusion of the CdTe crystals (6 mm diameter and 500 μm thick) was performed in an evacuated quartz ampoule for 30 min.

The CdTe crystals were mechanically polished and the mass loss was determined by weighting of the crystal after each step of polishing. The thicknesses of the abraded layers ranged between 2 μm and 20 μm . The number of ^{111}Ag atoms within each layer was determined by measuring the intensity of the 342 keV γ -line of the radioactive decay of ^{111}Ag with a Germanium well-detector.

Results

Figure 1 (top panel) shows the diffusion profile of sample #1 after implantation of 10^{10} Ag cm^{-2} with an energy of 80 keV and diffusion at 550 K. The measured concentration profile exhibits a depletion layer with a thickness of about 80 μm starting directly at the crystal surface. This region is followed by an asymmetric peak of the Ag concentration at a depth of about 110 μm . Under slightly changed conditions this experiment, which exhibited a peak concentration of only $2 \cdot 10^{12}$ Ag cm^{-3} , was repeated with a higher Ag concentration: A second crystal (sample #2) was implanted with a dose 100 times higher and with a slightly lower energy of 60 keV. The data in Fig. 2, presented at an enlarged depth scale, still show the depletion zone below the surface, which in this case extends over 10 μm . If the diffusion temperature is increased from 550 K to 800 K (sample #3), the data in Fig. 1 (bottom panel) show that the profile becomes symmetric over the entire crystal. The ^{111}Ag concentration in the central region of this crystal is almost constant at a value of 10^{14} cm^{-3} and decreases by one order of magnitude within a layer of about 100 μm towards both surfaces. It should be noted that a sample treated at the same temperature of 800 K but containing a significantly higher Ag concentration (sample #4 in Table 1), shows a profile that is nearly homogeneous at a concentration level of $5 \cdot 10^{18}$ cm^{-3} over the entire crystal.

A drastic effect is visible if, in addition, Cu is evaporated onto the ^{111}Ag implanted surface before diffusion annealing at 550 K (sample #5). The data in Fig. 3 show that in this crystal the ^{111}Ag atoms are nearly completely moved to the back (i.e. to the non implanted side) of the crystal. This observation can be explained by assuming a repulsive interaction between the Cu and Ag atoms which causes a diffusion of the Ag atoms to the other surface of the crystal. By comparing these data with the corresponding results at 550 K shown in Figs. 1 and 2, it could be stated that in Fig. 3 the depletion layer is extended over almost the whole crystal.

Discussion

The depletion layers of the ^{111}Ag profiles, visible in Figs. 1 and 2, cannot be explained by out-diffusion of ^{111}Ag during the cooling down process: There was neither a significant loss of the ^{111}Ag activity of the crystals nor a strong enrichment of ^{111}Ag atoms on the surface detectable after annealing of the crystals. In order to explain the depletion layer below the surface the existence of a repulsive effect for the Ag atoms is proposed, as is most drastically reflected by the data in Fig. 3. Motivated by the observed strong influence of the presence of Cu on the Ag diffusion profile, the reason for the repulsive effects in Figs. 1 and 2 can be assigned to the presence of extrinsic or intrinsic defects in the depleted layers of these crystals, probably to Cu. Considering the data in Fig. 1, a quantitative description of the measured ^{111}Ag profiles can be found semi-empirically by assuming a depth dependent drift velocity $v(x)$ of the Ag atoms. The corresponding drift-diffusion equations describing the Ag concentration c can be expressed by

$$j = -D \cdot \partial_x c + v(x) \cdot c \quad \text{and} \quad \partial_x j = -\partial_t c, \quad (1)$$

where j denotes the flux of Ag atoms through a plane parallel to the surface per time unit and D is the diffusion coefficient for Ag in CdTe. The symmetric Ag profile of sample #3 visible in Fig. 1 (bottom panel) seems to indicate the state of thermal equilibrium at the diffusion temperature of 800 K. The shape within the layer of 100 μm below each surface is determined by the balance between the inward directed drift velocity and the diffusion in a concentration gradient. In order to fit the boundary condition of a symmetric profile in thermal equilibrium, the velocity profile has to be an asymmetric function with respect to the centre of the crystal with thickness L . For fitting the data of sample #1 and sample #3 the drift velocity $v(x)$ was parameterised by the function

$$v(x) = -v_0 \cdot \alpha \cdot [\tanh(s \cdot (x - w)) + \tanh(s \cdot (x - L + w))] \quad (2a)$$

$$\text{with } 1/\alpha = \tanh(s \cdot w) + \tanh(s \cdot (L - w)), \quad (2b)$$

which is plotted as a dashed curve in both panels of Fig. 1. This function has the values $+v_0$ and $-v_0$ in the regions of width w neighbouring the two surfaces, is nearly zero in between, and the parameter s controls the transient between the different regions. Using this function, Eq. 1 was solved numerically. The ^{111}Ag concentration at $t=0$ is determined by the approximately Gaussian implantation profile of about 20 nm width close to $x=0$, and the boundary conditions are defined by a vanishing flux ($j=0$) of ^{111}Ag atoms at both surfaces of the crystal. The diffusion data of samples #1 and #3 were fitted by variation of the parameters D , v_0 , s , and w . The resulting fits (solid lines in Fig. 1) account in a satisfactory way for both diffusion profiles measured at 550 K and 800 K. In case of sample #1, the diffusion coefficient D and the drift velocity v_0 are determined to $D = 3 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and $v_0 = 0.2 \mu\text{m}/\text{s}$, whereas in case of sample #3 only the ratio $D/v_0 = 45 \mu\text{m}$ can be extracted, which is larger by a factor of 3 than in sample #1. Extrapolating to 550 K the diffusion coefficients for Ag in CdTe, which were determined by Wartlick et al. [3] in the range between 320 and 350 K ($D = D_0 \cdot \exp(-0.22 \text{ eV}/kT)$ with $D_0 = 6.5 \cdot 10^{-6} \text{ cm}^2/\text{s}$) a value of $6.3 \cdot 10^{-8} \text{ cm}^2/\text{s}$ is obtained, which is in good agreement with the value determined for D in sample #1. The different values of the quotient D/v_0 for samples #1 and #3 are plausible because of the different diffusion temperatures.

This quantitative description of the experimental data in Fig. 1, however, gives no information about the origin of the repulsive interaction acting on the Ag atoms since the used function $v(x)$ is not derived from a physical model. The cause of this interaction may be qualitatively explained by a repulsive interaction between Cu and Ag atoms, best seen in Fig. 3. Cu atoms seem to be present in almost all CdTe crystals as a residual contamination, indicated e.g. by the Cu^0X bond exciton frequently observed in PL investigations [6,7]. Thus, a connection between the repulsive interaction exerted on the Ag atoms and the Cu contamination in samples #1, #2, and #3, which were not intentionally doped with Cu, seems to be possible. The reduction of the depletion layer in Fig. 2 (sample #2) and the invisibility of this interaction in sample #4 is explained by the increasing Ag/Cu ratio in these samples, yielding Ag concentrations that significantly exceed the concentration of the residual Cu contamination. In contrast to the data in Fig. 1, the ^{111}Ag profile of sample #2 shown in Fig. 2 could not satisfactorily be fitted using the simple function of Eq. 2 for describing the drift velocity $v(x)$. This may reflect the physical nature of the repulsive interaction, which is expected to depend on the gradient of the Cu concentration and the concentration of Ag.

Finally, the ^{111}Ag diffusion data of sample #5 shown in Fig. 3 will be considered. The diffusion of Cu in CdTe was investigated e.g. by Woodbury and Aven, Panchuk et al., and Jones et al. [8,9,10]. Jones et al. used an evaporated Cu layer as diffusion source, similar to the conditions for Cu diffusion chosen in the present experiments, and they detected a slow and a

fast diffusing component of Cu. The diffusion coefficient D and the solubility c_s of the fast component are reported to be nearly independent on temperature in the range 450 to 600 K and are determined to $D = 3.3 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and $c_s = 10^{17} \text{ cm}^{-3}$, respectively. On the basis of the data presented by Jones et al., the Cu profile was calculated assuming an infinite Cu source and plotted in Fig. 3 (dashed line). A comparison with the Ag data shows that the Cu concentration obviously exceeds the Ag concentration over the entire crystal, except for a thin layer at the back of the crystal where most of the Ag atoms are accumulated. The nearly complete diffusion of the ^{111}Ag atoms to the back of the crystal, therefore, seems obviously to be caused by the repulsive interaction between Cu and Ag. It should be remarked that the diffusion of Cu and Ag in CdTe observed here might show up some similarities with the interaction of p-type dopants, i.e. of Zn and Cd, in InP reported by Tuck et al. [11]. In that experiment, the presence of Cd was found to increase the diffusion depth of Zn but, contrary to the present data, the presence of the diffusing Zn greatly increased the rate of out-diffusion of Cd from the semiconductor.

Conclusion

The presented data on the diffusion of Ag in CdTe are interpreted in the framework of a repulsive interaction between the diffusing Ag and Cu atoms. In crystals that were not intentionally doped with Cu, the residual concentration of Cu causes a drift of the Ag atoms towards the centre of the crystal which superposes the diffusion in the presence of a concentration gradient. The visibility of this interaction vanishes with increasing Ag concentration. Upon intentional co-diffusion of CdTe with Cu, however, the observed effect becomes more pronounced indicating that the presence of Cu atoms seems to be responsible for the observed repulsion of the Ag atoms. Within a semi-empirical model, quantitatively describing the diffusion data at 550 K and 800 K (Fig. 1), the diffusion coefficient of Ag in CdTe corresponding to a temperature of 550 K was determined. This value is in good agreement with extrapolated data of the temperature dependent diffusion coefficient published by Wartlick et al. [3]. Although the measured ^{111}Ag profiles can be understood qualitatively, on the basis of the present data a microscopic interpretation about the nature of the long range repulsive interaction between Cu and Ag can not be given yet.

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References

- [1] J.P. Chamonal, E. Molva, J.L. Pautrat, *Solid State Comm.* **43** (1982) 801.
- [2] M.A. Kovalets, N.I. Kuchman, E.S. Nikonyuk, I.P. Chiokan, and M.M. Shvydka, *Fizika i Khimiya Obrabotki Materialov* **21** (1987) 125
- [3] B.O. Wartlick, J.F. Barbot, and C. Blanchard, *Philosophical Magazine B* **75** (1997) 639
- [4] I. Lyubomirski, V. Lyakhovitskaya, R. Triboulet, and D. Cahen, *Journal of Electronic Materials* **26** (1997) 97
- [5] I. Lyubomirski, M.K. Rabinal, and C. Cahen, *J. Appl. Phys.* **81** (1997) 6684
- [6] B. Monemar, E. Molva, and L.S. Dang, *Phys. Rev. B* **33** (1986) 1134
- [7] J. Hamann, A. Burchard, M. Deicher, T. Filz, V. Ostheimer, F. Strasser, H. Wolf, ISOLDE Collaboration, and Th. Wichert, *Physica B* **273-274** (1999) 870
- [8] H.H. Woodbury and M. Aven, *J. Appl. Phys.* **39** (1968) 5485
- [9] O.E. Panchuk, V.I. Grystiv, and D.P. Belotskii, *Inorgan. Mater.* **11** (1988) 788
- [10] E.D. Jones, N.M. Stewart, and J.B. Mullin, *J. Cryst. Growth* **117** (1992) 244
- [11] B. Tuck, F.R. Shepherd, G. Kelly, and A. Margittai, *Semicond. Sci. Technol.* **15** (2000) 254

Table 1: Preparation conditions of the CdTe crystals used for the diffusion experiments. The diffusion times were always 30 min.

sample Nr.	Ag layer	energy	dose	Ag diffusion	Cu diffusion
#1	-	80 keV	10^{10} cm^{-2}	550 K	-
#2	-	60 keV	10^{12} cm^{-2}	550 K	-
#3	-	60 keV	10^{12} cm^{-2}	800 K	-
#4	30 nm	60 keV	10^{12} cm^{-2}	800 K	-
#5	-	80 keV	10^{10} cm^{-2}	550 K	550 K

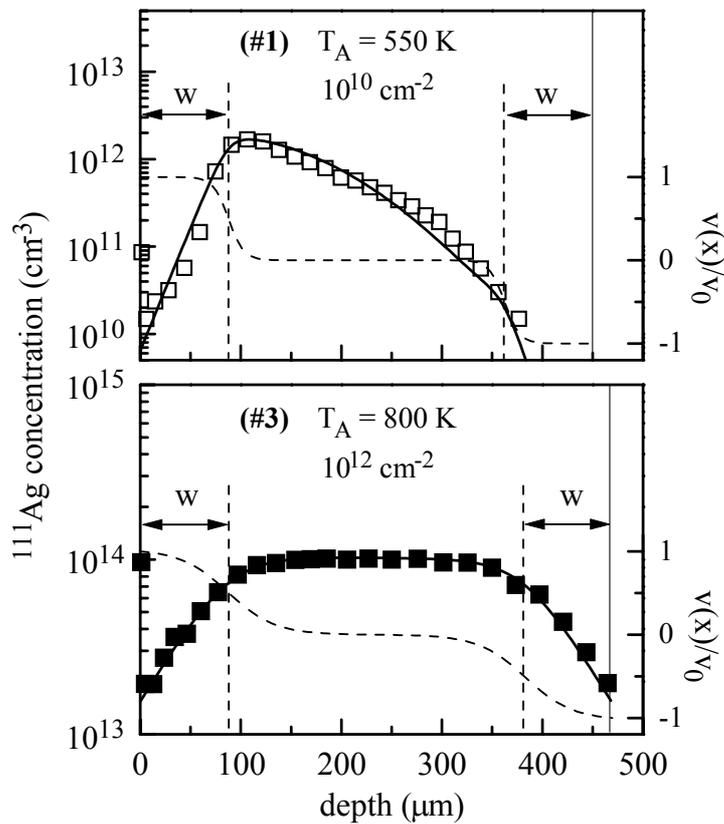


Fig. 1: ^{111}Ag profiles measured after annealing at 550 K (top) and 800 K (bottom). The dashed lines correspond to the right axes and show the drift velocity (Eq. 2) used for fitting the diffusion profiles. The vertical solid line marks the back of the CdTe crystal and the vertical dashed lines indicate the range of different drift velocities described by the parameter w in Eq. 2.

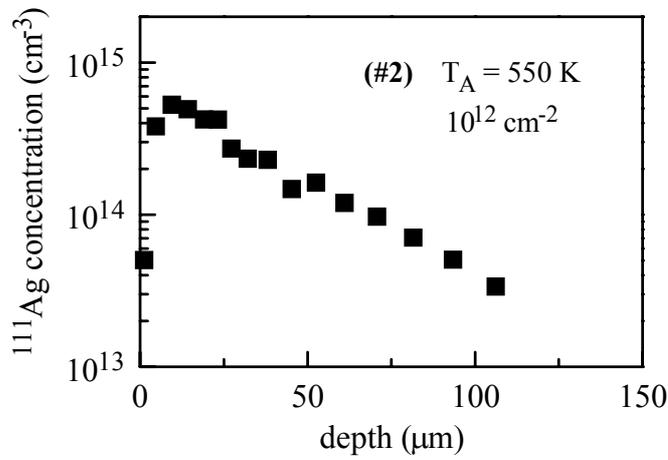


Fig. 2: ^{111}Ag profile measured after annealing at 550 K, but in contrast to Fig. 1 (top), a 100 times higher dose of ^{111}Ag was implanted. Note, the enlarged depth scale.

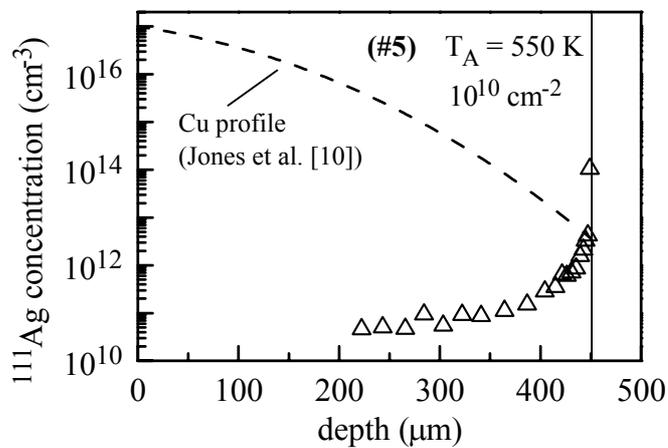


Fig. 3: ^{111}Ag profile measured after diffusing of Cu at 550 K. The dashed line shows the Cu profile, expected on the basis of data published by Jones et al. The vertical solid line marks the back of the crystal.