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Drift-Diffusion of Highly Mobile Dopants in CdTe

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Abstract. The diffusion of Ag in CdTe exhibits anomalous concentration profiles, which essentially reflect the profile of the deviation from stoichiometry. At a diffusion temperature of about 800 K, the Ag dopant atoms are present as charged interstitials. The deviation from stoichiometry at diffusion temperature substantially changes upon an external source of Cd atoms. Such an external source can be represented either by the vapor pressure from metallic Cd or by a Cd layer arising at the interface to an evaporated layer of Cu or Au. Also, the Co diffusion in CdZnTe is shown to be strongly affected by the presence of an external vapor pressure of Cd, but in a substantially different way compared to the Ag diffusion in CdTe.

1 Introduction

In most of all cases, the diffusion of dopant atoms into elemental and compound semiconductors leads to diffusion profiles that monotonously decrease with the distance from the source of the dopant [1]. In contrast, the diffusion of Ag and Cu in CdTe exhibits anomalous diffusion profiles depending on the external conditions during diffusion [2,3]: The shapes of the profiles are essentially determined by variations of the deviation from stoichiometry during diffusion, which are initiated by the external vapor pressure of Cd, acting as a source or drain of interstitial Cd defects. Since in a semiconductor, like CdTe, donor and acceptor defects can be present in different charge states, an inhomogeneous distribution of donors and acceptors generates an internal electric field, which, besides the concentration gradients, causes an additional driving force on charged defects. In the limit of low Ag concentrations ([Ag] < 10^{16} cm^{-3}), the Ag profiles obtained in CdTe upon different external Cd pressures during diffusion are well described by a model described in ref. [4], which, in addition, is outlined in section 4. It will be shown that also layers of metallic Cu or Au evaporated on the implanted surface generate a source of Cd atoms that influences drastically the Ag diffusion in CdTe. Finally, the occurrence of unusual diffusion profiles is not restricted to the dopants Ag and Cu as will be demonstrated using the example of Co diffusion in CdZnTe.

2 Experimental Details

The Ag diffusion experiments were performed with the radiotracer ^{111}Ag implanted into 800 or 500 µm thick CdTe crystals with an energy of 80 keV. The Co diffusion was investigated at a 500 µm thick CdZnTe (ca. 3% Zn) crystal after 60 keV implantation of the radiotracer ^{61}Co. Some CdTe samples were coated with a 20 nm Cu or 30 nm Au layer after ^{111}Ag implantation. In all experiments, the diffusion profiles were determined by mechanical polishing. The thickness of the respective abraded layer was determined by weighing the remaining crystal and the number of ^{111}Ag or ^{61}Co atoms within the abraded layer was determined by detecting the intensity of the emitted γ-radiation using a Ge well-detector.

3 Results

The Ag profile shown in Fig. 1 was obtained after diffusion at 828 K for 60 min under Cd pressure [2-5]. The Ag profile is symmetric with respect to the center of the crystal and is accompanied by two strongly Ag depleted layers with a width of about 300 µm towards both surfaces. (Note, that the temperature values of 800 K given in the earlier publications [2-5] had to be corrected to 828 K. As a consequence, the values of the diffusion coefficients and the deviations from stoichiometry differ from those given in ref. [4])
At a lower diffusion temperature of 570 K (30 min) the Ag profile becomes monotonously decreasing as expected on the basis of Fick's laws (open squares in Fig. 2a), but the shape of the Ag profile changes drastically, if 20 nm Cu were evaporated onto the implanted surface

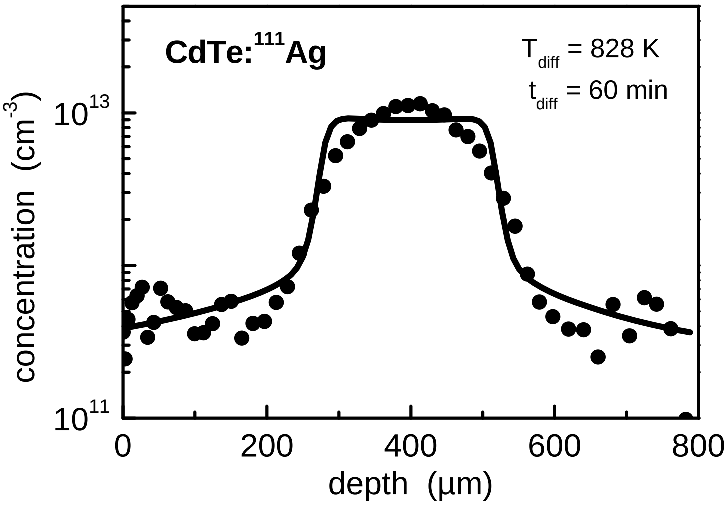
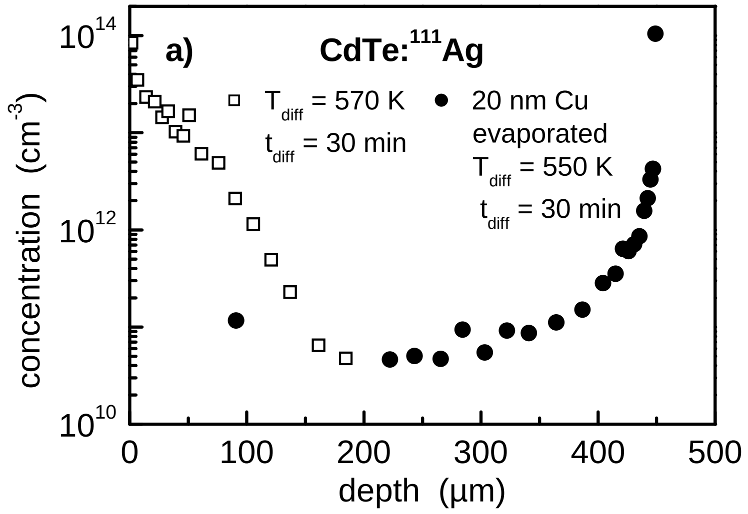


Fig. 1: ^{111}Ag profile in CdTe obtained after diffusion at 828 K for 60 min under Cd pressure. The solid line corresponds to a simulation according to the model described in sec. 4.

(a)



(b)

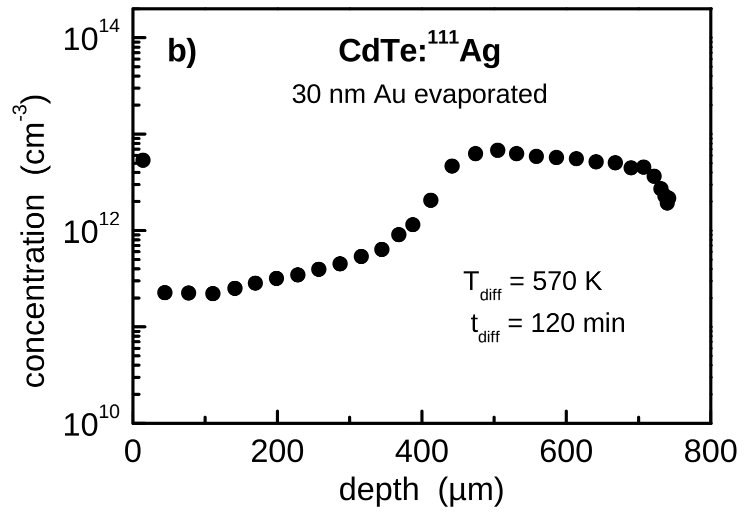


Fig. 2: ^{111}Ag profiles in CdTe measured after implantation of ^{111}Ag and evaporation of (a) a Cu layer (filled circles) and (b) a Au layer onto the implanted surface. In panel (a) (open squares) additionally the Ag profile obtained without evaporated metal layer is shown . Note the different thicknesses of the crystals in (a) and (b)

before annealing (550 K, 30 min; filled circles in Fig. 2 (a)) [5]. Obviously, the Cu layer causes a strong driving force on the implanted ^{111}Ag atoms directed towards the backside of the crystal where more than 70% of the Ag atoms reside in a layer of less than 10 µm. Similarly, but less pronounced is the effect of evaporating a 30 nm Au layer onto the surface (Fig. 2 (b)). Here, a depletion layer of 400 µm develops after 120 min diffusion time at 570 K, see ref. [5].

Fig. 3 shows two diffusion profiles that were obtained after implantation of ^{61}Co into CdZnTe: After diffusion under Ar atmosphere for 30 min at 800 K, the Co profile (open squares) extends up to about 10 µm into the crystal. In contrast, if the diffusion is performed under Cd pressure, the Co diffusion seems to be strongly enhanced because the profile reaches a depth of about 200 µm (filled circles). With the exception of the weakly pronounced depletion layer at 20 µm below the surface, the concentration is constant over a range of 150 µm followed by a decrease of the concentration ranging over 80 µm.

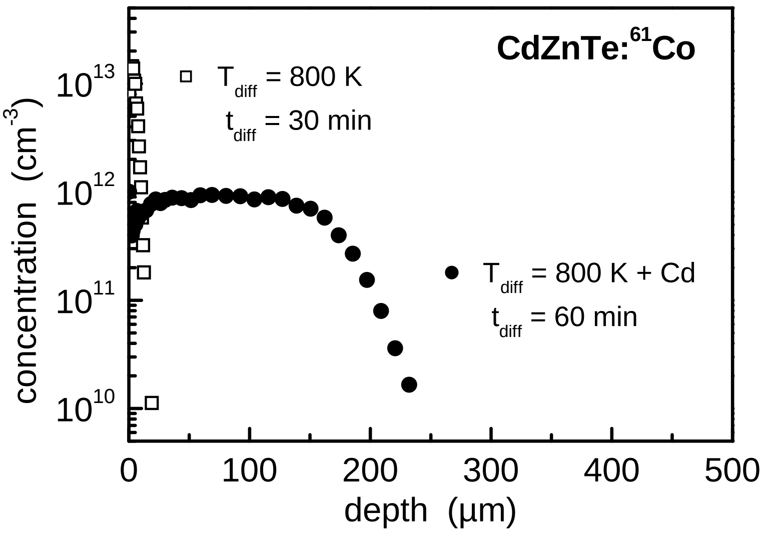


Fig. 3: ^{61}Co profiles measured after implantation and subsequent annealing under Ar atmosphere (open squares) and under Cd pressure (filled circles).

Obviously, the diffusion of Ag and Co strongly depends on the external conditions during diffusion, *i.e.*, on the external Cd pressure or on the presence of a metal layer on the implanted surface. Thereby, the evaporated Cu or Au layer seems to have qualitatively the same effect as an external vapor pressure of Cd, but at the chosen conditions the metal layers seem to be much more efficient and effective at significant lower temperatures. Since it has been shown that the external Cd pressure changes the deviation from stoichiometry of the host crystal [4] it is assumed that also the Cu or Au layer changes the deviation from stoichiometry.

4 Theoretical Description

In general, the concentration of each defect [Y_i] in a crystal is described by its formation energy $F(\mathrm{Y}_i)$ and chemical potential $\mu(\mathrm{Y}_i)$. In case of diluted systems, the concentration can be expressed as

$$\left[\mathrm{Y}_i\right] = C_{i,0} \cdot \exp\left(-\frac{F(\mathrm{Y}_i)}{k_\mathrm{B}T}\right) \cdot \exp\left(\frac{\mu(\mathrm{Y}_i)}{k_\mathrm{B}T}\right). \tag{1}$$

Here, $C_{i,0}$ denotes the density of lattice sites available for the incorporation for defect Y_i. Eq. (1) can be applied also to electrons and holes whereby the density of lattice sites available has to be replaced by the effective density of states of the conduction band (electrons) and valence band (holes). In this context, also electrons and holes are regarded as defects.

Defect reactions being in local thermal equilibrium are described by relations between their chemical potentials

$$\mathrm{Y}_i + \mathrm{Y}_j \rightleftharpoons \mathrm{Y}_k \qquad \mu(\mathrm{Y}_i) + \mu(\mathrm{Y}_j) = \mu(\mathrm{Y}_k). \tag{2}$$

The flux J of the defect Y_i is described by the Onsager flux equations [6,7]:

$$J(\mathrm{Y}_i) = -\sum\nolimits_j L_{ij} \cdot \frac{\mathrm{d}}{\mathrm{d}x} \mu(\mathrm{Y}_j), \tag{3}$$

i.e., it depends on the gradients of the chemical potentials of all defects involved and on the phenomenological coefficients L_{ij} with $L_{ij} = L_{ji}$ [6]. If the L-Matrix is diagonal, all defects obey the first Fick's law and the coefficients L_{ii} are identified as

$$L_{ii} = D\left(\mathrm{Y}_i\right)\cdot\left[\mathrm{Y}_i\right], \tag{4}$$

introducing the diffusion coefficients $D(\mathrm{Y}_i)$.

In the present case of Ag diffusion in CdTe, the defects considered are (i) the interstitial Cd_i donor, which can be present in three different charge states (Cd_i^0, Cd_i^+, Cd_i^{2+}) and at two non-equivalent interstitial sites, (ii) the interstitial Ag_i donor (Ag_i^0, Ag_i^+), which is also present at two non-equivalent interstitial sites, (iii) the substitutional $\mathrm{V_{Cd}}$ acceptor ($\mathrm{V_{Cd}^0}$, $\mathrm{V_{Cd}^-}$, $\mathrm{V_{Cd}^{2-}}$), (iv) the substitutional $\mathrm{Ag_{Cd}}$ acceptor ($\mathrm{Ag_{Cd}^0}$, $\mathrm{Ag_{Cd}^-}$), and (v) the free electrical carriers e^- and h^+. The two non-equivalent interstitial sites of the Cd_i defect can be distinguished in our model because the values of the respective formation energies are reported in the literature [8]; this information is not available in case of the Ag_i defect. The resulting defect reactions are

$$\mathrm{Ag_{Cd}^0} + Cd_i^0 \rightleftharpoons \mathrm{Ag}_i^0 \qquad \mu\left(\mathrm{Ag_{Cd}^0}\right) + \mu\left(\mathrm{Cd}_i^0\right) = \mu\left(\mathrm{Ag}_i^0\right) \tag{5a}$$

$$\mathrm{Ag}_i^0 + \mathrm{V_{Cd}^0} \rightleftharpoons \mathrm{Ag_{Cd}^0} \qquad \mu\left(\mathrm{Ag}_i^0\right) + \mu\left(\mathrm{V_{Cd}^0}\right) = \mu\left(\mathrm{Ag_{Cd}^0}\right), \tag{5b}$$

These reactions are well-known in the literature as the kick-out mechanism (5a) and the dissociative mechanism (5b), respectively [1]. The combination of eqs. (5a) and (5b) yields the annihilation of intrinsic defects:

$$\mathrm{V_{Cd}^0} + Cd_i^0 \rightleftharpoons 0 \qquad \mu\left(\mathrm{V_{Cd}^0}\right) + \mu\left(\mathrm{Cd}_i^0\right) = 0 \tag{6}$$

In addition, there have to be considered charge transfer reactions, which in case of Ag are

$$\mathrm{Ag}_i^0 + h^+ \rightleftharpoons \mathrm{Ag}_i^+ \qquad \mu\left(\mathrm{Ag}_i^0\right) + \mu\left(h^+\right) = \mu\left(\mathrm{Ag}_i^+\right) \quad \text{and} \tag{7a}$$

$$\mathrm{Ag_{Cd}^0} + e^- \rightleftharpoons \mathrm{Ag_{Cd}^-} \qquad \mu\left(\mathrm{Ag_{Cd}^0}\right) + \mu\left(e^-\right) = \mu\left(\mathrm{Ag_{Cd}^-}\right), \tag{7b}$$

In addition, the corresponding relations for the charge transfer in case of intrinsic defects have to be taken into account. For the annihilation of free carriers holds

$$e^- + h^+ \rightleftharpoons 0 \qquad \mu\left(e^-\right) + \mu\left(h^+\right) = 0, \tag{8}$$

In total, there are 12 different types of defects present which are connected by 9 relations between the corresponding chemical potentials. Consequently, the 12 defect concentrations are described by only three chemical potentials, which are chosen as $\mu_{Ag} = \mu(\mathrm{Ag}_i^0)$, $\mu_{Cd} = \mu(\mathrm{Cd}_i^0)$, and $\mu_F = \mu(e^-)$. Thereby, the chemical potential μ_F describes the difference of the actual Fermi-level to the intrinsic Fermi-level $\mu_i = E_\mathrm{g}/2 - \frac{3}{4}\cdot k_\mathrm{B}T\cdot\ln\left(m_e^*/m_h^*\right)$, where m_e^*, m_h^*, and E_g, are the effective masses of electrons and holes, and the bandgap energy, respectively. Corresponding to the three chemical potentials, there are three concentration quantities, which do not change upon defect- and charge transfer-reactions. These quantities are

$$[\mathrm{Ag}] = [\mathrm{Ag}_i] + [\mathrm{Ag_{Cd}}] \tag{9a}$$

$$[\Delta C] = [\mathrm{Cd}_i] - [\mathrm{V_{Cd}}] - [\mathrm{Ag_{Cd}}] \tag{9b}$$

$$[Cq] = 2\left[\mathrm{V_{Cd}^{2-}}\right] + \left[\mathrm{V_{Cd}^-}\right] + \left[\mathrm{Ag_{Cd}^-}\right] + \left[e^-\right] - 2\left[\mathrm{Cd}_i^{2+}\right] - \left[\mathrm{Cd}_i^+\right] - \left[\mathrm{Ag}_i^+\right] - \left[h^+\right], \tag{9c}$$

which describe the total Ag concentration [Ag], the deviation from stoichiometry $[\Delta C]$, and the charge density by $\rho = \mathrm{e}\cdot[Cq]$. Since the charge density ρ has to obey the Poisson equation, there remain only two independent chemical potentials, μ_{Ag} and μ_{Cd}, whereas μ_{F} is calculated by solving the Poisson equation.

The formation energies of charged defects $\mathrm{Y}^{z\pm}$ are calculated on the basis of the formation energies of the respective neutral defects Y^0 by

$$F\left(\mathrm{Y}^{z\pm}\right)=F\left(\mathrm{Y}^{0}\right)\mp\sum_{j=1}^{z}E_j\left(\mathrm{Y}\right)-k_{\mathrm{B}}T\cdot\ln\left(g_{\mathrm{Y}}^{z}/g_{\mathrm{Y}}^{0}\right). \tag{10}$$

Here, the upper and lower signs correspond to donor- and acceptor-defects, respectively. $E_j(\mathrm{Y})$ represents the j-th energy level of the defect Y in the band gap measured from the intrinsic Fermi-level μ_i and g_{Y}^{z} is the degeneracy factor of the z-th energy level of the defect Y. In this context, the intrinsic Fermi-level μ_i can be identified with the formation energy of the free carriers. The concentration of available lattice sites is $C_0 = 1.48 \cdot 10^{22}$ cm^{-3} for each non-equivalent interstitial site and for substitutional defects, where C_0 is the density of CdTe molecules in a CdTe crystal. The formation energy of the $\mathrm{Ag}_{\mathrm{Cd}}$ defect, as defined in eqn. 1 describes the complete exchange of a Cd host atom by a Ag impurity atom; therefore, this energy differs from the energy used in refs. [4,8], where it defines the occupation of an already present Cd vacancy by a Ag atom.

For describing the experimental Ag diffusion data presented here, it is assumed that the flux of the defect Y is determined by the gradient of the chemical potential $\mu(\mathrm{Y})$. In case of charged defects $\mathrm{Y}^{z\pm}$, additionally the gradient of μ_{F}, which describes the internal electric field generated by the distribution of the charged defects, causes a driving force on the defect $Y^{z\pm}$. The resulting drift current is described by

$$J_{\mathrm{drift}}\left(\mathrm{Y}^{z\pm}\right)=\mp\frac{z}{k_{\mathrm{B}}T}\cdot D\left(\mathrm{Y}\right)\cdot\left[\mathrm{Y}^{z\pm}\right]\cdot\frac{\mathrm{d}\mu_{\mathrm{F}}}{\mathrm{d}x}. \tag{11}$$

Here, the diffusion coefficient $D(\mathrm{Y})$ is assumed to be independent of the respective charge state. For the concentrations [Ag] and [ΔC] the resulting fluxes are

$$J_{\mathrm{Ag}}=-\left(D\left(\mathrm{Ag}_i\right)\cdot\left[\mathrm{Ag}_i\right]+D\left(\mathrm{Ag}_{\mathrm{Cd}}\right)\cdot\left[\mathrm{Ag}_{\mathrm{Cd}}\right]\right)\cdot\frac{\mathrm{d}\mu_{\mathrm{Ag}}}{\mathrm{d}x}+D\left(\mathrm{Ag}_{\mathrm{Cd}}\right)\cdot\left[\mathrm{Ag}_{\mathrm{Cd}}\right]\cdot\frac{\mathrm{d}\mu_{\mathrm{Cd}}}{\mathrm{d}x} \tag{12a}$$

$$\begin{aligned}J_{\Delta C}&=+D\left(\mathrm{Ag}_{\mathrm{Cd}}\right)\cdot\left[\mathrm{Ag}_{\mathrm{Cd}}\right]\cdot\frac{\mathrm{d}\mu_{\mathrm{Ag}}}{\mathrm{d}x}\\&\quad-\left(D\left(\mathrm{Cd}_i\right)\cdot\left[\mathrm{Cd}_i\right]+D\left(\mathrm{V}_{\mathrm{Cd}}\right)\cdot\left[\mathrm{V}_{\mathrm{Cd}}\right]+D\left(\mathrm{Ag}_{\mathrm{Cd}}\right)\cdot\left[\mathrm{Ag}_{\mathrm{Cd}}\right]\right)\cdot\frac{\mathrm{d}\mu_{\mathrm{Cd}}}{\mathrm{d}x}\end{aligned} \tag{12b}$$

Finally, for simulating the concentration profiles of [Ag] and [ΔC] the fluxes in eqns. (12a) and (12b) have to obey the continuity equation.

5 Discussion

The solid line shown in Fig. 1 is the result of a simulation using the model introduced before in context with ref. [4]. It turns out that the data are well described if the model assumes that the Ag dopant essentially is present as Ag_i^+ at the diffusion temperature of 828 K. For the Ag_i defect a donor level of less than 560 meV below the conduction band edge is obtained and for the parameter $\Delta F_{\mathrm{Ag}} = F(\mathrm{Ag}_{\mathrm{Cd}}^0) + F(\mathrm{V}_{\mathrm{Cd}}^0) - F(\mathrm{Ag}_i^0)$, describing the stability of the Ag atom on substitutional lattice sites, the energy is smaller than 1.5 eV. From the height of the calculated profile the initial deviation from stoichiometry is determined to $[\Delta C]_{\mathrm{ini}} = -3.3 \times 10^{16}$ cm^{-3}. The final deviation from stoichiometry $[\Delta C]_{\mathrm{fi}} = 3 \times 10^{15}$ cm^{-3}, reached at the surface of the crystal, is determined by the external vapor pressure of Cd and is calculated on the basis of the data published by Grill *et al.* [8] and Berding [9]. Finally, the diffusion coefficients of the participating defects are determined to $D(\mathrm{Ag_i}) = 2 \times 10^{-7}$ cm^2/s, $D(\mathrm{Cd_i}) = 7 \times 10^{-7}$ cm^2/s, and $D(\mathrm{V_{Cd}}) = 10^{-9}$ cm^2/s. The direct diffusion of Ag on substitutional sites was neglected, *i.e.*, in the calculations the diffusion coefficient $D(\mathrm{Ag_{Cd}})$ was set to zero. The positions of the steep gradients of the Ag profile indicate the transitions from Cd rich to Te rich material, which act as *pn*-junctions. A detailed discussion of the different model parameters is given in [10].

As shown in Fig. 3, also the diffusion of Co in CdZnTe is strongly influenced by the external vapor pressure of Cd applied during diffusion: During annealing under Ar pressure, the Co dopant diffuses only about 10 µm into the crystal. In contrast, if an external Cd source is present the penetration depth of the Co atoms into the crystal increases drastically to about 200 µm. This depth is comparable with the width of the depletion layer observed after Ag diffusion in CdTe under similar conditions (see Fig. 1). Since this position was identified as a *pn*-junction, the Co atoms might penetrate into the host material just up to that *pn*-junction. A qualitative explanation might be found assuming that Co atoms, at least in Cd rich material, are present as highly mobile, negatively charged interstitial atoms. It will be subject of future experiments to examine this assumption.

The Ag depth profile in Fig. 1 essentially reflects the depth profile of the deviation from stoichiometry $[\Delta C]$ obtained after heating under Cd pressure at the respective temperature. About the center of the crystal, the initial value $[\Delta C]_{\mathrm{ini}}$ is still present, whereas at the surfaces $[\Delta C]_{\mathrm{fi}}$ is reached corresponding to the equilibrium value that is determined by the actual external Cd pressure. Thus, the external Cd pressure acts as a source of Cd atoms that change ΔC. In case of the data obtained after evaporation a Cu or Au layer onto the surface (see Fig. 2), however, no external Cd pressure was applied, even though a very strong driving force seems to act on the Ag atoms which is caused by the metal layer. A qualitative explanation of this experimental observation is found if it is assumed that the Cu or Au layer extracts Te atoms from the CdTe crystal leaving a Cd rich layer at the interface. The quantitative differences observed for the Cu and Au layer might be connected to the different efficiencies of Cu and Au to extract Te atoms from the CdTe crystal. In any case, the density of Cd atoms available at such an interfacial source, formed at the boundary between metal layer and semiconductor, is expected to be much higher than that generated by a gaseous source like in the case of diffusion of Ag under Cd pressure. As a consequence, the propagation of the change of the deviation from stoichiometry should happen much faster in case of the interfacial source than in case of the gaseous source, what is in agreement with the experimental observations. A quantitative description, however, seems to exhibit a serious problem because knowledge about the density of interfacial Cd atoms as a function of time during the diffusion process would be necessary. However, it should be noted that corresponding to the initial deviation from stoichiometry of -3.3×10^{16} cm^{-3} two to three monolayers of Cd atoms would be sufficient to fill up all vacancies in a 500 µm thick crystal.

6 Conclusions

The unusual diffusion behaviour of Ag in CdTe is described quantitatively by a theoretical model presented here. The Ag dopant at the diffusion temperature of 828 K is present as highly mobile Ag_i^+ ions. As a consequence, the Ag profile essentially reflects the profile of the deviation from stoichiometry. The deviation from stoichiometry is substantially modified, if an external source of Cd is present, which can be represented either by a gaseous source or by an interfacial Cd layer generated by an evaporated layer of Cu or Au that extracts Te atoms out of the CdTe host crystal. Also the diffusion of Co is strongly influenced by the presence of a external gaseous Cd source. The shape of the profile, observed in Cd rich material at 800 K, indicates an incorporation of Co as negatively charged ions.

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