Intrinsic Defects in ZnSe, ZnTe, and CdS doped with Li

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Abstract

Doping of the II-VI semiconductors CdS, ZnSe, and ZnTe with Li atoms was investigated by PAC spectroscopy. During isothermal Li diffusion experiments the formation of cation vacancies was observed, which was detected by the formation of A-centres involving the probe ^{111}In. The dependence of the concentration of A-centers on temperature and time, observed in ZnTe, is described by a thermodynamical model, from which the diffusion coefficient of the cation vacancy and the solubility of Li in ZnTe is deduced.

Introduction

II-VI semiconductors are technologically interesting materials for realizing optoelectronic devices [1]. The introduction of dopants, however, often leads to the effect of self-compensation via the formation of intrinsic defects, having a charge opposite to the introduced dopant atoms. The electrical carrier concentration, therefore, is often significantly lower than the dopant concentration. In some II-VI semiconductors, this process can nearly completely suppress either *p*-type doping (ZnS, ZnSe, CdS, CdSe) or *n*-type doping (ZnTe). The diffusion of the potential acceptor Li into II-VI semiconductors causes the formation of cation vacancies as observed in perturbed angular correlation (PAC) experiments [2]. The lack of *p*-type conductivity after Li diffusion in most of the II-VI semiconductors is possibly caused by the formation of electrically inactive pairs, which consist of substitutional and interstitial Li atoms [3]. In ZnTe, however, by Martin et al. [4] Li atoms were reported to be incorporated substitutionally up to 80 % after diffusion. The formation of cation vacancies caused by the diffusion of Li atoms was observed via the formation of A-centres, consisting of the donor probe ^{111}In$_M$ and the acceptor-like cation vacancy V_M (M = Zn, Cd) [2,5]. The fraction of ^{111}In atoms, being involved in A-centres, is a measure for the concentration of V_M generated by Li diffusion. The dependence of the concentration of A-centres on temperature and time during Li diffusion yields information about thermodynamical parameters like the solubility of Li and the diffusion coefficients of Li and V_M. In this report, a quantitative analysis of isothermal Li diffusion experiments, performed on ZnTe, is given.

Experimental details

A defect, like the cation vacancy, close to the radioactive probe atom ^{111}In gives rise to a defect-specific electric field gradient (efg). After the decay of the isotope ^{111}In to ^{111}Cd, the interaction of the nuclear quadrupole moment Q with this efg generates three frequencies in the PAC time spectrum, which is described by

$$R(t) = A_2 \left[f \cdot \left(S_0 + \sum_{n=1}^{3} S_n \cos \omega_n t \right) + (1-f) \right] \tag{1}$$

The largest component of the efg, V_{zz}, is usually expressed by the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$, which is proportional to ω_1. Additionally, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ is deduced from the frequency ratio ω_2/ω_1 and satisfies the condition $0 \bullet \eta \bullet 1$. The factor f denotes the relative fraction of ^{111}In atoms, which are associated with the efg, and the coefficient $A_2 = -0.14$ describes the spatial anisotropy of the emission of the second γ-ray with respect to the first one. A more detailed description of the PAC spectroscopy is found elsewhere [6].

For the diffusion of the radioactive ^{111}In atoms into the samples, ^{111}InCl$_3$ and a small amount (ca. 1 mg) of the respective chalcogen element were sealed within an evacuated quartz ampoule, which was heated at 1070 K for 90 min. For CdS samples, a diffusion depth in the order of a few μm was determined by tracer experiments [5] and and a similar depth is estimated for the other II-VI semiconductors.

The diffusion of Li atoms was performed by heating the ^{111}In doped sample with metallic Li in an evacuated quartz ampoule. Isochronal diffusion experiments were performed in the temperature range between 550 K and 900 K, using a diffusion time of 30 min. The isothermal diffusion experiments on ZnTe samples were performed at temperatures between 700 K and 800 K in a time range up to 10 h, divided into time intervals of 30 min. After diffusion, the quartz ampoule was quenched into a water bath in order to preserve the thermodynamical conditions of the respective diffusion temperature and time.

Results and Discussion

The efg, measured in the II-VI semiconductors MX (M = Zn, Cd; X = S, Se, Te) after diffusion of Li atoms, are almost identical to those observed after diffusion with the respective chalcogen element, except in case of ZnTe [7]. In ZnTe, no significant formation of a corresponding defect structure is observed after Te diffusion; nearly all of the ^{111}In probe atoms are located on perfectly unperturbed cation sites, as shown by the almost constant value of R(t) = -0.13 in the PAC spectrum (fig. 1c). The diffusion of Li atoms into ZnTe, however, leads to the formation of a defect structure, which is characterised by an efg similar to those observed in the other II-VI samples in case of A-centres [2,5,7]. PAC spectra, obtained before and after diffusion of Li atoms, are compared in fig. 1 (a-d) for ZnSe and ZnTe samples.

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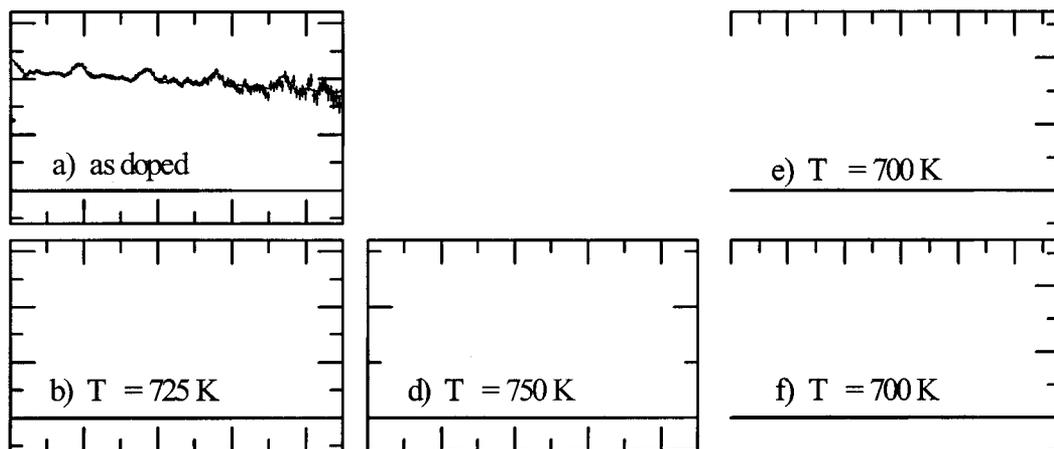
Fig. 1: R(t) spectra of ZnSe (a,b) and ZnTe (c-f) samples. The samples were diffused with the probe [111]In (a-d) or implanted with the probe [77]Br (e,f). The spectra before (a,c,e) and after (b,d,f) diffusion with Li atoms are compared.

In ZnTe, an assignment of the observed efg to $In_{Zn}-Li_{Zn}$ pairs can not completely be excluded on the basis of PAC experiments performed with the probe ^{111}In, but the similarity of the efg to that caused by A-centres in CdTe suggests the formation of $In_{Zn}-V_{Zn}$ pairs. Performing PAC experiments with the donor probe [77]Br, which was implanted into ZnTe at the ISOLDE facility at CERN, yields a defect structure after annealing the sample at T_A = 700 K, as shown in fig. 1e. It is interpreted to be caused by the formation of $Br_{Te}-V_{Zn}$ pairs as a consequence of the implantation damage. After diffusion of Li atoms into the sample at T_d = 700 K, no change of the measured efg was observed (fig. 1f), rather a slight increase of the fraction of $Br_{Te}-V_{Zn}$ pairs could be seen. This indicates that $Br_{Te}-Li_{Zn}$ pairs were not formed, even though the binding energy of a nearest neighbour $Br_{Te}-Li_{Zn}$ pair is expected to be larger than that of the next-nearest neighbour pair $In_{Zn}-Te-Li_{Zn}$. Therefore, also in the case of ZnTe doped with ^{111}In, the formation of $In_{Zn}-V_{Zn}$ pairs rather than of $In_{Zn}-Li_{Zn}$ pairs is concluded to occur after diffusion of Li.

Fig. 2 shows a strong increase of the fraction of In_M-V_M pairs within a narrow temperature range of about 100 K at a temperature of 650 K (CdS), 700 K (ZnSe), and 750 K (ZnTe). The sample and the metallic Li source were at identical temperatures. The comparison with a reference

sample (open squares) shows that the strong increase of the pair formation, and thereby of the formation of cation vacancies, is correlated with the diffusion of Li atoms into the sample. Thus, isothermal diffusion experiments, performed in this temperature range, should yield information about the formation of V_M and the diffusion of Li atoms into the sample. The corresponding data, obtained for ZnTe samples, are plotted in fig. 3. They exhibit a temperature dependence of the equilibrium value $f_\bullet$ of the concentration of A-centres and of the time constant τ, characterising the increase of f. This increase with diffusion time is qualitatively explained by the penetration of the Li induced cation vacancies into the doping profile of the ^{111}In atoms. The equilibrium value $f_\bullet$ and the time constant τ are expected to be temperature dependent via the temperature dependence of the solubility of Li atoms in ZnTe and should depend on the concentration and the diffusion coefficient of the cation vacancy V_{Zn}.
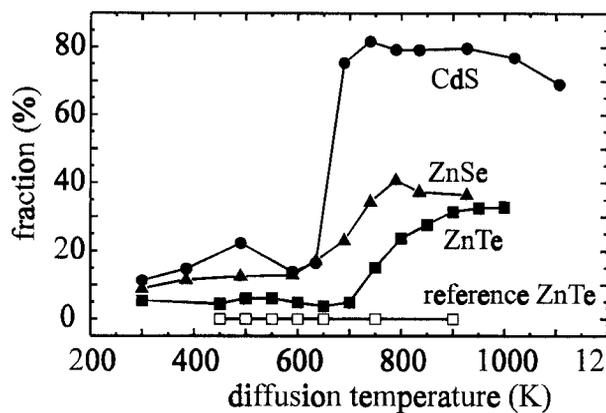

Fig. 2: In_M-V_M formation during isochronal Li diffusion in CdS, ZnSe, and ZnTe for a diffusion time of 30 min. The reference sample was identically treated but without the addition of Li.
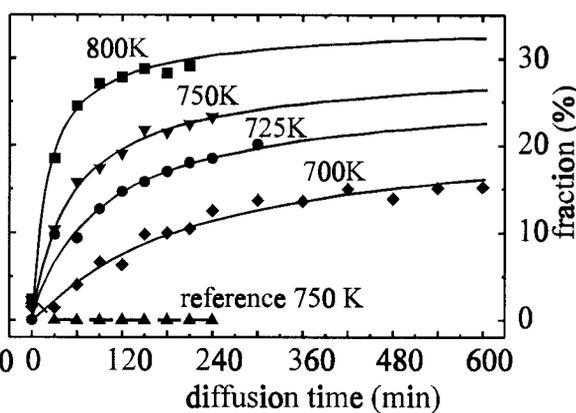
Fig. 3: In_M-V_M formation during isothermal Li diffusion in ZnTe for different temperatures. The solid lines are fits to the data as described by eq. (6).

The diffusion of Li in ZnTe is reported to occur by two mechanisms, a fast one, corresponding to the diffusion along dislocations and grain boundaries and a slow one, corresponding to the substitutional diffusion via cation vacancies [4]. Since the ^{111}In probe atoms are located on unperturbed substitutional cation sites after doping, no significant effect from the fast component is expected to be observed by PAC experiments. The diffusion coefficient for the substitutional diffusion of Li is $D(T) = 2.9 \cdot 10^{-2} \cdot \exp(-1.22 \text{ eV}/kT)$ [4]. From the Sievert law, the solubility of Li in ZnTe is expected to be proportional to the external vapour pressure of Li and to a Boltzmann factor containing the heat of solution E_s [8]. Therefore, the solubility of Li in ZnTe is expressed by $[Li]_s = N \cdot \exp(-(E_v-E_s)/kT)$, where N is a pre-factor and E_v is the heat of evaporation of Li metal. The cation vacancies, required for Li diffusion, can, in principle, be generated either thermally or catalytical due to the presence of Li vapour at the surface. PAC experiments, performed on ZnTe samples that were thermally treated at temperatures up to 900 K, show no formation of In_{Zn}-V_{Zn} pairs (open squares in fig. 2). Therefore, the catalytically generation of cation vacancies at the surface, induced by Li vapour is concluded. Since the cation vacancies migrate into the crystal in front of the substitutionally diffusing Li atoms, an excess of V_{Zn} is available for the formation of A-centres with the In atoms. Taking into account the formation and dissociation of In_{Zn}-V_{Zn}, the local concentration of A-centres at a depth x is described by the following rate equation

$$\frac{d}{dt}[In-V]_x = -\nu \cdot e^{-E_m/kT} \cdot \left(e^{-E_b/kT}[In-V]_x - \Omega \cdot \left([In]_x - [In-V]_x\right) \cdot \left([V]_x - [In-V]_x\right) \right) \quad (2)$$

Here, ν is the vibration frequency of a cation neighbouring a cation vacancy V_M, E_m and E_b are the migration energy and the binding energy of V_M to the donor In, and Ω describes the trapping volume of an In atom. Assuming equilibrium conditions regarding the formation of A-centres, the explicit time dependence vanishes and eq. (2) can be solved to obtain the local concentration of

In_{Zn}-V_{Zn} pairs. The fraction f of In_{Zn}-V_{Zn} pairs, measured by PAC, corresponds to the integral of $[In-V]_x$ over the overlap of the concentration profiles of In_{Zn} and V_{Zn}, divided by the total number of In atoms.

The concentration profile of the ^{111}In probe atoms is expected to be Gaussian, because the offered amount of about 10^{11} probe atoms represent a finite diffusion source; the profile remains unchanged by the Li diffusion because of the significantly lower temperatures used. Since the Li atoms were supplied from a piece of metallic Li (ca. 5 mg), representing an infinite diffusion source, the concentration profile of Li atoms is described by a complementary error function, which is also expected for the profile of the cation vacancies. Therefore, the concentration of V_{Zn}, available for the formation of A-centres, is obtained by subtracting the depth profile of Li, from the profile of the cation vacancies. The normalised concentration profiles are described by

$$g_{In}(x) = \frac{[In]_x}{[In]_{x=0}} = e^{-\frac{x^2}{4 \cdot L^2}} \quad \text{and} \quad g_v(x,t) = \frac{[V]_x}{[V]_{x=0}} = \frac{1}{1-\varepsilon}\left(\text{erfc}\left(\frac{x}{2L}\sqrt{\frac{\tau_v}{t}}\right) - \varepsilon \cdot \text{erfc}\left(\frac{x}{2L}\sqrt{\frac{\tau_{Li}}{t}}\right)\right). \quad (3)$$

The time constants $\tau_v \equiv L^2/D_v$ and $\tau_{Li} \equiv L^2/D_{Li}$ describe the diffusion profiles of V_{Zn} and Li_{Zn} in the crystal, expressed by the diffusion depth L of the In profile, and contain the diffusion coefficients of V_{Zn} and Li_{Zn}, respectively. From the In diffusion length L, being in the order of a few μm, the concentration $[In]_{x=0} \approx 10^{15}$ cm^{-3} at the surface is estimated. The parameter ε describes the fraction of V_{Zn} that was originally diffused into the crystal and subsequently occupied by Li atoms, thereby forming Li_{Zn}. Assuming a trapping radius of about 5 lattice constants, corresponding to $\Omega = 10^{-19}$ cm^3, and a binding energy of $E_b = 0.3$ eV, similar to that determined for In_M-V_M pairs in CdS and ZnSe [2], the relation

$$a \equiv \frac{e^{-E_b/kT}}{\Omega \cdot [In]_{x=0}} \gg 1 \qquad (4)$$

holds. With the abbreviation $b \equiv [V]_{x=0}/[In]_{x=0}$ the local concentration of A-centres is approximated by

$$[In-V]_x = [In]_{x=0}\frac{g_{In}(x) \cdot g_v(x,t)}{a/b + g_v(x,t)} \qquad \text{resulting in} \qquad (5)$$

$$P(t) = \frac{\int[In-V]_x \, dx}{\int[In]_x \, dx} = \frac{2}{\sqrt{\pi}}\int\frac{g_{In}(y) \cdot g_v(y,t)}{a/b + g_v(y,t)} dy \quad \text{with} \quad y \equiv \frac{x}{2L} \qquad (6)$$

The data of the isothermal Li diffusion experiments presented in fig. 3 were fitted with the function P(t) of eq. (6), using as free parameters the time constant τ_v and the ratio a/b. The time constant τ_{Li} was calculated, using the diffusion coefficient D_{Li}, given above. For all temperatures, ε was kept constant, whereby the results were not significantly affected by the choice of ε, being in the range of $10^{-3} < 1 - \varepsilon < 10^{-1}$. Further, a consistent fit to all data was possible for a diffusion length L of the In atoms in the range 2 μm < L < 10 μm. The solid lines in fig. 3 correspond to the parameters $1 - \varepsilon = 10^{-2}$ and L = 5 μm. The fitted parameters τ_v and a/b are collected in the Arrhenius plot in fig. 4. From the temperature dependence of the time constant τ_v the diffusion coefficient of V_{Zn} is determined as $D_v = 2.8(1) \cdot 10^{-2} \cdot \exp(-1.22(1) \text{ eV}/kT)$, which is almost identical to D_{Li}. The second fit parameter can be expressed by the solubility of Li atoms as

$$b/a = \Omega \cdot [V]_{x=0} \cdot e^{E_b/kT} = \Omega \cdot (1-\varepsilon) \cdot [Li]_{x=0} \cdot e^{E_b/kT} = \Omega \cdot (1-\varepsilon) \cdot N \cdot e^{-(E_v - E_s - E_b)/kT} \qquad (7)$$

The temperature dependence of b/a in fig. 4 yields the pre-factor $N = 1.45 \cdot 10^{22}$ cm^{-3} and the heat of solution $E_s = 1.12$ eV, using the value $E_v = 1.64$ eV, extracted from the temperature dependence of the vapour pressure of Li [9]. The temperature dependent solubility of Li atoms in ZnTe is expressed by $[Li]_{x=0} \equiv [Li]_s = 1.4(1) \cdot 10^{22} \cdot \exp(-0.52(1) \text{ eV}/kT)$. The quoted errors are determined by

the uncertainty of ε. The pre-factor N and the heat of solution E_s are additionally affected by the uncertainty of the trapping volume Ω and the binding energy E_b, which are estimated to be in the order of $\Delta\log(\Omega) = \bullet 1$ and $\Delta E_b = \bullet 0.1$ eV, respectively.

Corresponding experiments in ZnSe and CdS show a qualitatively similar behaviour but are strongly affected by an additional formation of thermally produced cation vacancies. In order to perform a quantitative analysis of the data obtained during isothermal Li diffusion, first, the cation vacancies formed during ^{111}In diffusion have to be removed before starting the diffusion experiments.
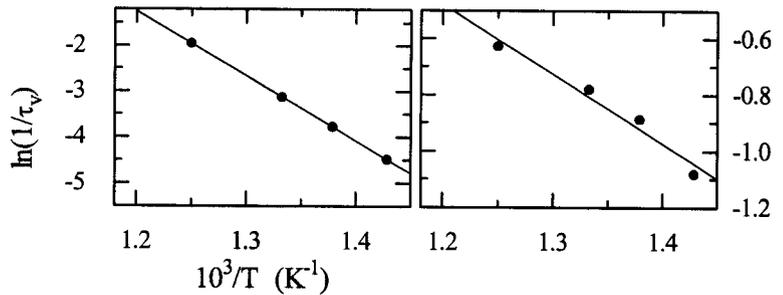

Fig. 4: Arrhenius plot of the reciprocal time constant $1/\tau$ and the ratio b/a, representing the fit parameters of the discussed model.

Conclusions

The diffusion coefficient of the cation vacancy V_{Zn} and the solubility of Li atoms in ZnTe were deduced from PAC experiments, performed within an isothermal Li diffusion sequence. The almost identical diffusion coefficient of Li_{Zn} and V_{Zn} are not believed to be accidental, but seem to reflect specific properties of the diffusion mechanism. The diffusion process of Li in ZnTe is obviously initialised by the catalytic formation of V_{Zn} at the surface, which starts to diffuse into the crystal and are subsequently occupied by Li atoms. The experimental data can not satisfactory be fitted, if the diffusion coefficients D_{Li} and D_v are assumed to be identical (eq. (3) becomes independent on ε) or if the formation of In_{Zn}-Li_{Zn} pairs instead of In_M-V_M pairs is assumed (limes $\varepsilon \to 0$ and replacing V_{Zn} by Li_{Zn} in eq. (3)). The diffusion of V_{Zn} happens slightly faster than that of Li which occupies about 99 % of the originally produced V_{Zn} defects. The solubility of Li is determined by the concentration of the originally produced cation vacancies. The pre-factor $N = 1.4(1)\cdot10^{22}$ is plausible in that the dissolution of a solid at infinite temperatures is understood as the formation of a vacancy concentration, being identical to the concentration of host atoms.

Acknowledgement

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ZnSe:^{111}In   ZnTe:^{111}In   ZnTe:^{77}Br

a) as doped

b) T_d = 725 K

c) as doped

d) T_d = 750 K

e) T_A = 700 K

f) T_d = 700 K

t(ns)   t(ns)