



Experimental evidence of the self-compensation mechanism in CdS

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Abstract

Microscopic origin of full electrical compensation of donor doped CdS was analyzed with perturbed angular correlation and Hall-effect measurements. Single crystals were implanted with radioactive ¹¹¹In and stable ¹¹⁵In ions. Total In concentration ranged from 10¹⁶ to 10²⁰/cm³. A strong correlation was observed between electrical self-compensation and the formation of (In_{Cd}-V_{Cd}) pairs (A centers) as a result of thermal annealings. It is shown that the presence of In donors during thermal treatment under the S pressure provokes spontaneous formation of (doubly) ionized cation vacancies [V_{Cd}]. During cooling, these vacancies form pairs with In donors (A center), which compensate the rest of the donors, leading to highly resistive material. The experiments presented provide direct evidence for self-compensation: doped crystals spontaneously create just a matching concentration of native point defects needed to compensate foreign doping atoms electrically. This holds for over four orders of magnitude of In concentrations. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Doping difficulties and compensation of dopants is a notorious problem in wide band-gap semiconductors. The microscopic mechanism of de-activation of dopants is generally difficult to discern due to the scarcity of methods which would give clear

and quantitative information about the chemical nature, local structure, and concentrations of suspected compensating defects, and to correlate them with electrical properties (e.g. Ref. [1]). Perturbed angular correlation (PAC), where applicable, offers a quantitative account of all probe atoms in various lattice sites and surroundings [2]. The combination of PAC and electrical measurements can provide for each of these sites a quantitative correlation between free carrier concentration, thus enabling assessment of doping (in)efficiency.

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In this paper the origin of de-activation of In donors in CdS was analyzed with PAC and Hall-effect measurements on the same set of samples, in order to connect macroscopic and microscopic information on doped samples. The mechanism of full electrical compensation, which occurs when crystals are treated thermally under the S pressure, has been explained at the atomic level revealing causes of de-activation of In donor over a wide range of In concentrations.

2. Experimental details and measurement techniques

Undoped commercial ('Crystal', Berlin) CdS single crystals were used as a starting material. Implantations were carried out at room temperature (RT) with 350 keV $^{111}\text{In} + ^{115}\text{In}$ ions in a non-channeling direction. Dose range was 10^{11} – $10^{15}/\text{cm}^2$, corresponding to peak concentrations from 10^{16} to $10^{20}/\text{cm}^3$ in the implanted layer. Implanted samples were annealed for 10 min in 50 or 100 K steps up to 1073 K, in quartz ampoules under the S pressure of approximately 2 atm. After quenching to RT, an additional 10 min annealing was performed at 423 K to maximize pairing of defects.

The resistivity and Hall mobility were measured in the 20–300 K temperature range in a standard Van der Pauw configuration. PAC spectroscopy detects the interaction of the quadrupole moment of the nuclear probe with the local electric field gradient (EFG) induced by the immediate neighborhood of the probe atom [2]. The EFG causes hyperfine splitting of an excited state of ^{111}Cd created by the decay of ^{111}In , which can be described by the quadrupole coupling constant ν_Q and the asymmetry parameter η (where $0 \leq \eta \leq 1$). Each set of PAC parameters, ν_Q and η , unambiguously labels a particular, well-defined probe-atom-defect configuration allowing its easy identification under varying experimental conditions. The PAC spectrum [2] $R(t)$ reflects the perturbations due to EFGs (expressed by nuclear transition probabilities) and the fraction f of probe atoms exposed to the EFG. By fitting the measured $R(t)$, the PAC 'signatures' (ν_Q and η) for different

configurations were established as well as the fraction of the probe atoms involved in each of them.

3. Results

Fig. 1 shows characteristic PAC spectra obtained after annealing at $T_a = 973$ K. Each spectrum consists of three different EFGs, indicating three different surroundings of In atoms: Site 1 is characterized by $\nu_Q = 7.4$ MHz and no asymmetry ($\eta = 0$). This PAC 'signature' belongs to the

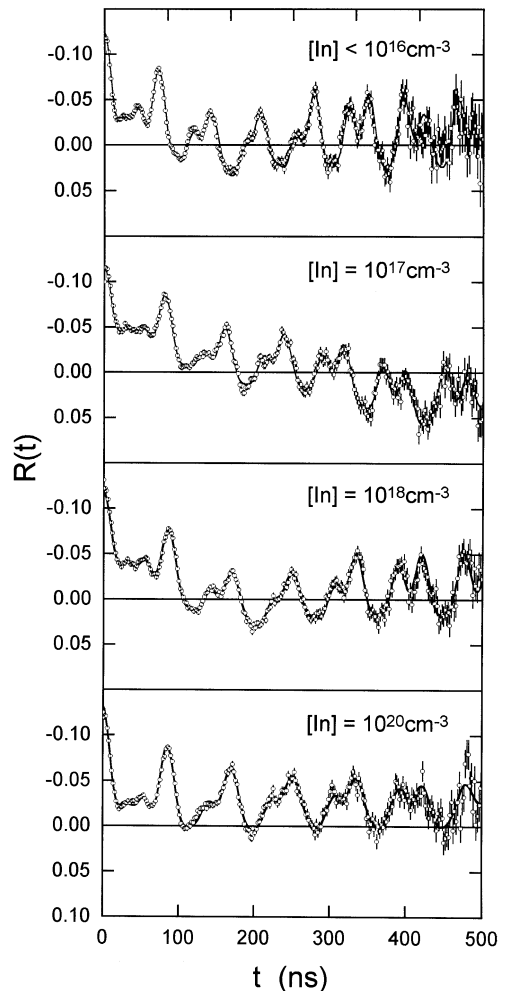


Fig. 1. The PAC spectra, $R(t)$, measured after implantation with different In doses and annealing at 923 K under S pressure. In concentrations range from $\leq 10^{16}$ to $10^{20}/\text{cm}^3$.

substitutional In_{Cd} in an undisturbed surrounding [2–4]. Sites 2 and 3 are characterized by two very close frequencies, $\nu_{\text{Q}} = 72$ MHz, $\eta = 0.35$, and $\nu_{\text{Q}} = 79$ MHz, $\eta = 0.21$. We have assigned [4] these two PAC signals to pairs between a substitutionally placed In atom and a cadmium vacancy, V_{Cd} , in the next-neighbor position, $(\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}})$, i.e. to the A center. The two close EFGs result from the slightly different distances between In_{Cd} and V_{Cd} placed in or out of the basal plane in the hexagonal CdS (Sites 2 and 3), respectively. Such an assignment has been widely accepted and it facilitated the assignment of analogous PAC signals observed later in other II–VI compounds [2]. It is particularly important that spectra obtained for In concentrations, $[\text{In}]$, between 10^{16} and $10^{20}/\text{cm}^3$ are hardly distinguishable, indicating that the same defect configurations have practically the same relative intensities over the whole range of $[\text{In}]$. The relation of total $[\text{In}]$ and concentration of In atoms in both unperturbed In_{Cd} and paired $(\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}})$ configurations is shown in Fig. 2 (concentrations of Sites 2 and 3 are summed up). Obviously, concentrations of both In configurations follow closely the total $[\text{In}]$. Note particularly that $[\text{V}_{\text{Cd}}]$ changes dramatically due to the presence of In, since all samples were otherwise treated identically.

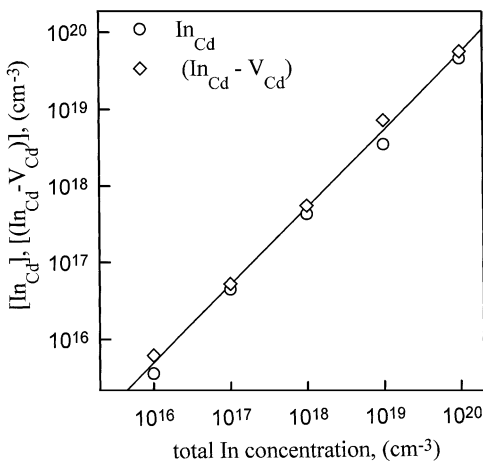


Fig. 2. Concentrations of free substitutional In atoms, $[\text{In}_{\text{Cd}}^+]$ (\circ), and paired In atoms, $[(\text{In}_{\text{Cd}}^+ - \text{V}_{\text{Cd}}^-)^-]$ (\diamond), as a function of total implanted In concentration, after 10 min annealing at 1073 K under S pressure. Straight line depicts $y = [\text{In}]/2$ function.

Electrical measurements on undoped and unannealed samples showed a decrease in conductivity from a relatively high value before thermal treatment ($\approx 0.3/\Omega$ cm; free electron concentration, n , in low $10^{16}/\text{cm}^3$) down to an unmeasurable low electrical conductivity ($< 10^{-12}/\Omega$ cm) for annealing under S pressure at 923 K and above. Despite doping, the implanted layer had also unmeasurably low conductivity after the same thermal treatment over the whole range of $[\text{In}]$, thus indicating the complete electrical compensation of all In donors even for the highest implantation dose.

4. Discussion

Electrical measurements show that annealing under the S pressure introduces p-type compensating defects in just as high concentrations as needed to completely annihilate the electrical activity of implanted In donors. The PAC measurements on the same samples demonstrate that the concentrations of undisturbed substitutional In_{Cd} and $(\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}})$ pairs are practically the same even for the highest $[\text{In}]$. Since in compensated material (Fermi level close to the middle of the band gap) the In_{Cd} atoms are undoubtedly single donors, and electrical measurements indicate that they are completely neutralized, the compensating species $(\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}})$ has to be a single acceptor. Therefore, the charge state of V_{Cd} can be safely determined as doubly negative.

Combination of PAC (Figs. 1 and 2) and electrical results shows that the CdS crystal thermally treated under the S pressure spontaneously creates the proper matching concentration of native point defects needed to compensate incorporated In donors. In the process of compensation, approximately half of the donors are directly neutralized (passivated) by pairing with V_{Cd} , forming the $(\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}})$ acceptors. The as-formed A centers compensate the rest of the spatially remote, unpaired donors, leading to a highly resistive, fully compensated material. Pairing occurs during cooling from high T (or low- T annealing after quenching) since Cd vacancies are mobile down to about 400 K [2]. Results indicate that at high T , under our experimental conditions, for CdS it is energetically more

favorable to create a native defect than a free electron (due to the large band gap and high ionicity). Hence, the concentration of cation vacancies is self-regulated and depends directly on the actual In concentration. The result explains at the microscopic level the de-activation of donors in S-annealed CdS, observed in electrical measurements decades ago [5]. The results also confirm the validity of the basic concept of the original model of self-compensation, proposed by Mandel [6], which assumes that the presence of dopants provokes spontaneous formation of oppositely charged native vacancies. However, a very important difference to Mandel's model is revealed: it is not the isolated native vacancy that is actually doing the compensation at RT, as assumed in the model, but rather the A center. The findings in this study agree well with the growing belief that isolated point defects, including vacancies, generally recombine during cooling from high T , since they have rarely been detected at RT, except under special conditions, such as electron or neutron irradiation, etc. (e.g. Ref. [1]). The findings are also in accordance with the experimental evidence (e.g. Ref. [7]) and theoretical predictions (e.g. Ref. [8]) that vacancies created at high T , can survive in considerable concentrations at RT if paired with dopants. Furthermore, up to now the A center has been detected with electron paramagnetic resonance, EPR, in ZnS, ZnSe, ZnTe and CdTe (e.g. Ref. [7]), although quantitative correlation with electrical properties, particularly over a wide range of dopant concentrations, is still missing. Taking into account the similarities between CdS and other wide-band semiconductors, the presented microscopic picture of the spontaneously formed compensating native defects is most likely valid for other II–VI's doped with group-III donors but probably not over such a wide range of donor concentrations. The methodology used in this work could be applied directly in the same way to other Cd-VI compounds doped with In donors (this is the ideal dopant/compound combination since the daughter isotope of ^{111}In is ^{111}Cd , i.e. a host atom) and, with some caution, to Zn compounds. It could provide quantitative and microscopic determination/identification of compensating species as well as doping limits for thermal treatments under various conditions.

It is also interesting that none of the other usual mechanisms for dopant de-activation interferes over the whole range of In donor concentrations. Namely, any fraction of misplaced In atoms, like In atoms at interstitial, antisite or irregular positions would be visible as a new signal in the PAC spectrum. Similarly, some other compensation/de-activation mechanisms such as possible lattice relaxation around the doping In atom, formation of a new phase containing a fraction of the In atoms, etc. would also be observed by creating an additional characteristic PAC 'fingerprint'. Nothing of the kind was detected up to concentrations $[\text{In}] = 10^{20}/\text{cm}^3$.

5. Conclusion

Quantitatively and at the microscopic level, we have demonstrated that spontaneously created A center deactivates dopants in the In-implanted CdS thermally treated under the S pressure. This very same mechanism limits the electrical conductivity over a very wide range of four orders of magnitude of dopant concentrations. It is shown that during the high T annealings under the S pressure the defects required for compensation, doubly negatively charged cadmium vacancies, are being created in the concentrations that are just needed for full electrical compensation.

Acknowledgements

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