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Compensating defects and electrical activation of donors in CdS

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Abstract

Electrical deactivation of donors in CdS was studied by using Perturbed $\gamma\gamma$ Angular correlation (PAC) spectroscopy and temperature dependence of Hall mobility, resistivity, and free-carrier concentration. PAC spectra and electrical properties were monitored as a function of thermal treatment either under S or Cd pressure in a temperature range from RT to 1073 K. For samples annealed above 800 K under S pressure, Hall effect showed increased electrical compensation whereas PAC detected spontaneous creation of cadmium vacancies, V_{Cd}, via the formation of $(In_{Cd}–V_{Cd})$ pairs. The increase of the concentration of compensating acceptors, determined from electrical measurements, precisely correlates with the increase of the concentration of $(In_{Cd}–V_{Cd})$ pairs found by means of PAC. In contrast to that, thermal treatment under Cd pressure up to 1073 K does not provoke the formation of compensating native defects up to [In] $> 10^{19}/cm^3$.

Keywords: Compensation; Native defects; CdS; PAC; Hall effect

1. Introduction

Although doping problems and limits are among the main restraining factors for broader applications of the exceptional potentials of II–VI semiconductors, the microscopic causes of these difficulties still remain generally unknown. The main causes, reviewed recently [1], are claimed to be the spontaneous formation of native defects and/or pairs, the lattice relaxation around the doping atom resulting in the formation of compensating deep localized levels, mid-gap pinning of the Fermi level, the amphoteric behavior of some dopants, or the low solubility of others.

Indium is potentially an excellent donor to render CdS highly conductive (and hence promising for n-type side of the p–n junction or heterojunction) but its electrical activation depends strongly on thermal treatment conditions [2]. A microscopic explanation of these differences has only recently started to emerge [3]. The radioactive isotope ^{111}In enables the use of perturbed $\gamma\gamma$ angular correlation (PAC) spectroscopy, a powerful technique which gives information about the immediate surroundings of In probe atoms in the crystal. Each specific atomic configuration and surroundings of ^{111}In is unambiguously labeled by a characteristic electric field gradient (EFG) which is described by two parameters: the hyperfine interaction strength, ν_Q, and the asymmetry parameter η [4]. In this paper, we shall demonstrate that compensating acceptors, which cause electrical deactivation of donors (as revealed by electrical measurements), are being formed in the same concentrations as cadmium vacancies (as deduced from PAC), thus proving that this native defect plays a crucial role in electrical properties of the donor-doped CdS for a very wide range of In concentrations.

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2. Experimental details and measurements techniques

Commercial, undoped n-CdS single crystals were implanted at room temperature (RT) with 350 keV ^{111}In + ^{115}In ions in a non-channeling direction with doses ranging from 1.3×10^{11} to 1.3×10^{16}/cm^2 [3]. Both virgin and implanted samples were annealed for 10 min in 50 or 100 K steps up to 1073 K, either under Cd or S pressure. The free-electron concentration, n, and Hall mobility, μ_H, were measured from 20 to 300 K in a standard Van der Pauw configuration. After each annealing step experimental data for n were fitted using expression [5]:

$$n(n+[N_A])/([N_D]-n-[N_A]) = gN_C\exp(-E_D/kT) \quad (1)$$

with donor ionization energy E_D, concentration of donors, $[N_D]$, and acceptors, $[N_A]$, treated as fitting parameters. N_C is the effective conduction band-edge density of states and g is the degeneracy factor [5].

To explore the experimentally determined T-dependence of μ_H, all potentially relevant scattering mechanisms [6] were taken into account and the total Hall mobility, μ_H, was then calculated by applying Matthiesen's rule

$$1/\mu_H = 1/\mu_{po} + 1/\mu_{dp} + 1/\mu_{pe} + 1/\mu_N + 1/\mu_I, \quad (2)$$

where μ_{po}, μ_{dp}, μ_{pe}, μ_N and μ_I denote scattering-limited mobility by optical polar phonons, deformation potential acoustic phonons, piezoelectric scattering, neutral impurities, (N_N), and ionized impurities, (N_I), respectively. Each specific mobility was calculated by using corresponding formulae [6] and constants appropriate for CdS [2,5,7].

A PAC spectrum $R(t)$ was taken after each annealing step. From the fit of $R(t)$, the fractions of ^{111}In in different atomic configurations/surroundings were determined, each distinguished by its characteristic PAC 'signature' (ν_Q and η).

3. Results

Fig. 1 depicts the temperature dependence of the free-electron concentration, $n(T)$, of undoped CdS samples (with residual effective donor concentration in 10^{16}/cm^3 range) as a function of thermal treatment under either S or Cd vapor pressure. For Cd annealed sample practically no changes in $n(T)$ were observed from RT up to $T_a = 1073$ K (only the last curve is shown). On the other hand, for the S-annealed sample, changes were small up to $T_a = 773$ K, but above $T_a = 873$ K the slope increased significantly and n drastically decreased. For higher annealing steps n becomes immeasurably low and is estimated to be less than 10^4/cm^3.

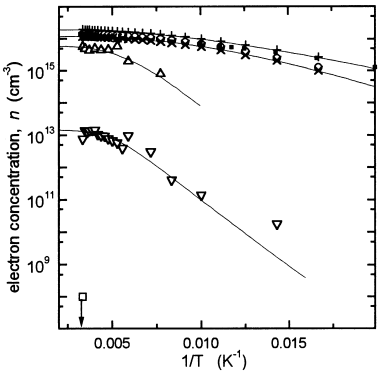

Fig. 1. Temperature dependence of the free-carrier concentration, n, after subsequent annealing under S pressure at T_a = RT (+), 573 K (○), 773 K (×), 823 K (△), 873 K (▽), and 923 K (□). $n(T)$ for the sample annealed under Cd pressure after $T_a = 1073$ K (■) is also shown. Full lines show the best fits according to Eq. (1).

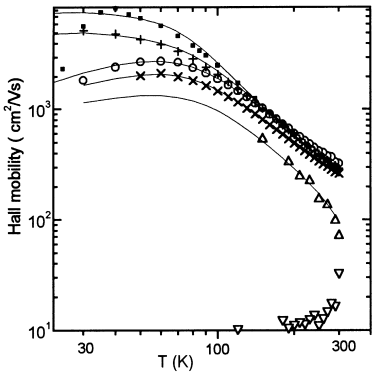

Fig. 2. Temperature dependence of the Hall mobility, μ_H, for the same samples and annealing conditions shown in Fig. 1. Symbols refer to the same T_a as in Fig. 1. Full lines show the calculated mobility, μ_H, following Eq. (2).

Hall mobility, $\mu_H(T)$, (Fig. 2) shows similar trends – small changes up to $T_a = 873$ K, and considerable, although much less dramatic, decrease of μ_H for higher T_a.

Several characteristic PAC spectra for a sample implanted with ^{111}In (1.3×10^{11}/cm^2) are shown in Fig. 3. All implantation-induced damage becomes completely annealed already after $T_a = 573$ K, and all of the In probe atoms are positioned in a single surrounding, distinguished by the characteristic PAC parameters $\nu_Q = 7.4$ MHz, and $\eta = 0$ (Site 1), which has been identified as substitutional In on Cd sites, In_{Cd} [8]. All probe atoms remain at In_{Cd} sites in unperturbed surroundings (Fig. 3a) up to $T_a \cong 800$ K independently of the annealing conditions.

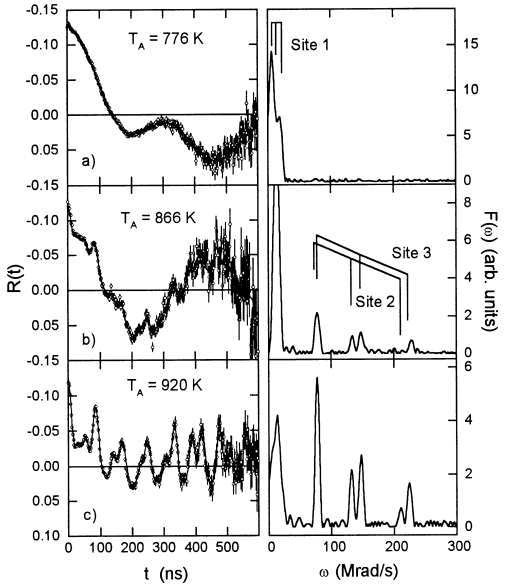

Fig. 3. PAC spectra (left) and their Fourier transforms (right) of In-implanted CdS after annealings up to 920 K under S pressure. The annealing temperature is indicated for each spectrum.

After annealing above 800 K under S pressure (Fig. 3b), two additional EFGs appear, assigned to (In_{Cd}–V_{Cd}) pairs [8] and characterized by a pair of frequencies, $\nu_Q = 72.4$ MHz with $\eta = 0.35$ (Site 2), and $\nu_Q = 78.7$ MHz with $\eta = 0.21$ (Site 3), respectively [4,8]. At higher T_a the fraction of (In_{Cd}–V_{Cd}) pairs becomes dominant although the signal belonging to In_{Cd} remains always present (Fig. 3c). We have observed a very similar behavior for higher In doses, up to In peak concentrations of $10^{20}/cm^3$ in the implanted layer. In those samples the fractions of pairs also similarly increased with the increase of T_a above 800 K. Above $T_a \cong 900$ K the fractions of pairs level up at around 50–70%, while the rest of the In atoms (30–50%) remains on Site 1 [3]. If the peak concentration of In exceeded $10^{20}/cm^3$, In started to precipitate into a second phase inside the CdS crystal [3].

The Cd annealed samples behaved differently: the PAC spectra with the single frequency 7.4 MHz (like in Fig. 3a) was obtained after each annealing step up to $T_a = 1073$ K. Furthermore, practically the same PAC spectrum was obtained for higher implantation doses as well, up to In peak concentrations of $10^{19}/cm^3$. For even higher doses, In started to precipitate into the second phase [3].

4. Discussion

The full lines in Fig. 1 are the results of fits of $n(T)$ using the Eq. (1). For $T_a = RT$, the E_D calculated from the fit is 27 meV, which is a very reasonable value for a shallow donor in the concentration range of $10^{16}/cm^3$ [2,5,7]. The increase of the annealing temperature up to 773 K does not induce virtually any change in E_D, indicating that the same shallow donors govern the electrical properties. The apparent small increase of the slope results from the small decrease of the effective donor concentration ($[N_D]_{eff} = [N_D] - [N_A]$) [2,5]. Above $T_a = 823$ K this shallow level becomes completely ionized i.e. all its electrons are trapped by compensating acceptors. The Fermi level is then lowered down to the next donor level deeper in the gap, which is, according to the fit, positioned at 70 meV below the conduction band. Above $T_a = 873$ K the same level still dominates the temperature dependence of n, but the concentrations $[N_D]$ and $[N_A]$ become very similar, primarily due to the stronger increase of $[N_A]$. Above $T_a = 923$ K, n becomes immeasurably low, indicating that the Fermi level is lowered much further down, close to or at the middle of the band-gap, due to the complete compensation of practically all donors by acceptors.

Fits of Eq. (2) to the experimental Hall mobility data are shown as full lines in Fig 2. The calculation showed that $\mu_{dp}(T)$ is unimportant throughout the whole T range. Similarly, μ_N is also insignificant, since unreasonably high concentrations of neutral scattering centers (above $10^{17}/cm^3$) would be needed to appropriately limit the maximal μ_H, and still the decrease of experimental μ_H observed at lower T_a could not be reproduced. Hence, this mechanism can be discarded as well. It was determined that at higher T optical phonons and piezoelectric scattering limit the mobility, while the maximum of $\mu_H(T)$ and its decrease at lower temperatures is limited by ionized impurities scattering, $\mu_I = A \cdot T^{3/2}/[N_I]$ (A is approximately a constant [5]). It was found that the $[N_I]$ values obtained from the fit to $\mu_H(T)$ were quite close to the sum of ($[N_D] + [N_A]$), determined independently from fitting of $n(T)$.

The agreement between measured μ_H and calculated μ_H breaks down for very high compensation (above $T_a = 873$ K, Fig. 2), since μ_H becomes rather low, and an unreasonable change of the material parameters in the expressions for μ_{po} and μ_{pe} would be needed to obtain a good fit. A considerable lowering of the mobility is often encountered in measurements of semi-insulating samples, ascribed to and convincingly explained by potential fluctuations [6]. Namely, when n is very low, any potential fluctuation becomes 'visible' since it affects/disrupts the continuity of the practically empty conduction band, thus lowering the measured mobility. In fact, the strong decrease of the mobility observed even at RT, provides independent proof that S annealing produces semi-insulating CdS samples.

The summary of the essential PAC, electrical experimental and calculated results for the $[N_D]_{eff.} \cong (10^{16}/cm^3$ donor level are given in Fig. 4 for S annealed samples.

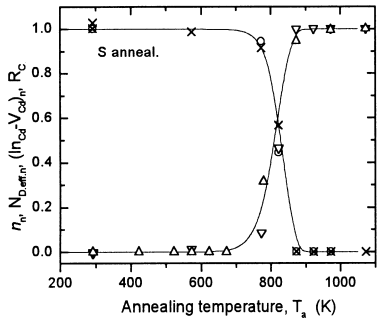

Fig. 4. Dependence of PAC and electrical properties (normalized values) of *n*-CdS annealed under S pressure (initial $[N_D]_{eff,RT} \cong 10^{16}/cm^3$) on the annealing temperature: n_n (○) – measured free-electron concentration normalized to its initial value at RT; $N_{D,eff,n}$ (×) – calculated effective donor concentration normalized to its initial value at RT; $(In_{Cd}-V_{Cd})_n$ (△) – fractions of pairs normalized to their saturating value at high T_a;(▽) – calculated compensation ratio, $R_C = 1 - ([N_D] - [N_A])/[N_D]$.

Above ≅800 K the $(In_{Cd}-V_{Cd})$ pairs appear and their fraction increases with higher T_a at the expense of the fraction of In_{Cd}. This change is closely matched with the increase of compensation, calculated from the fits of $n(T)$. The dynamics of the increase of $(In_{Cd}-V_{Cd})$ fraction, however, precisely correlates with the decrease of experimentally determined n, as well as with the decrease of the concentration of remaining donors, $[N_D]_{eff.}$. The fact that the sample becomes semi-insulating above $T_a \cong 800$ K means that not only the In_{Cd}^+ donors but also all other donors are deactivated. Since PAC showed that In donors become compensated by pairing with spontaneously formed V_{Cd} acceptors, it seems plausible that the other donors are being compensated by the analogous mechanism.

The electrical measurements of the In-implanted layer ([In] up to $10^{20}/cm^3$) were also done after annealing at 923 K under S pressure, i.e. after the substrate was converted to semi-insulating (Fig. 1). Again, very low n (lower than $10^8/cm^3$) was obtained, pointing out to the full compensation of all In donors. Obviously, S annealing creates just a matching concentration of V_{Cd} to fully compensate foreign donors, indicating that the same compensation mechanisms deactivate donors over the range of 4 orders of In concentrations. This finding offers the experimental proof at a microscopic level of the self-compensation mechanism by spontaneously created native defects [3].

5. Conclusion

The electrical activation of donors in CdS was studied by using Perturbed γγ angular correlation (PAC) spectroscopy and temperature dependence of Hall mobility and electrical resistivity. It has been found that donors become electrically deactivated after thermal treatment under S pressure. The increase of the concentration of compensating acceptors, determined from the electrical measurements (temperature dependence $n(T)$ and $\mu_H(T)$) exactly correlates with the increase of the concentration of $(In_{Cd}-V_{Cd})$ pairs, as determined from PAC. This correlation identifies cadmium vacancies, which are created spontaneously under S pressure above 800 K, as native defects responsible for the electrical deactivation of donors in CdS. Only for $[In] > 10^{19}/cm^3$–$10^{20}/cm^3$, In starts to precipitate into other phases within CdS.

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References

[1] U.V. Desnica, Prog. Cryst. Growth Charact. Mater. 36 (1998) 291.
[2] H.W. Woodbury, Phys. Rev. B 9 (1974) 5188 and 5195.
[3] U.V. Desnica, R. Magerle, I.D. Desnica-Frankovic, M. Deicher, A. Burchard, Phys. Rev. Lett., submitted for publication.
[4] Th. Wichert, Th. Krings, H. Wolf, Physica B 185 (1993) 297.
[5] J.L. Boone, G. Cantwell, J. Appl. Phys. 57 (1985) 1171.
[6] D.C. Look, Electrical Characterization of GaAs Materials and Devices, Wiley, New York, 1989.
[7] K. Morimoto, M. Kitagawa, T. Toshida, J. Crystal Growth 59 (1982) 254.
[8] R. Magerle, M. Deicher, U. Desnica, R. Keller, W. Pfeiffer, F. Pleiter, H. Skudlik, Th. Wichert, Appl. Surf. Sci. 50 (1991) 169.