



Study of microscopic mechanisms of electrical compensation of donors in CdS by fast diffusors (Cu, Ag, or Au)

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Abstract

The goal of this study was to identify microscopic causes of the extensive changes in electrical properties observed in CdS crystal when doped with some fast-diffusers (FD), Cu, Ag or Au. The compensation of donors and the dynamics of in-diffusion was quantitatively determined by $C-V$ measurements, whereas the changes at the atomic level were followed by perturbed angular correlation (PAC) spectroscopy. The penetration of FDs, as deduced from $C-V$, correlated well with changes observed in PAC, which manifest as new defects and/or as the increase of the concentration of $(V_{Cd}-In_{Cd})$ pairs. Arguments are given that the new defects observed by PAC in CdS:Ag belong to $(In_{Cd}^+-V_{Cd}^{2-}-Ag^+)^{\circ}$ and similar complexes in Cu. No indication of such complexes was observed in Au doped CdS. In CdS: Au practically all donors are passivated directly by pairing with V_{Cd} trapped at the nearest Cd site, whereas in Ag or Cu-doped CdS most of the donors are electrically compensated from the distance by FD_{Cd} acceptors. Our results suggest a complex microscopic mechanism by which the FD in-diffusion into CdS creates highly compensated semi-insulating material. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Direct band gap II–VI semiconductors are very promising for realizing efficient diode lasers and light-emitting diodes over the visible portion of the spectrum, efficient solar cells, X-ray and gamma-detectors, and a number of other applications. However, the persistent technological problems — control of electrical properties being the most puzzling — still hinders a wider use of these materials.

Fast diffusors from the IB group, like Cu, Ag or Au, are important impurities or dopants in all semiconductors and in II–VI compounds in particular. It has been observed that they diffuse much faster in II–VI's at relatively low temperatures than they do in Si, Ge or III–V's [1],

usually acting detrimentally on a number of desired properties, often in an uncontrollable way. The lowest temperatures at which diffusion coefficients in CdS monocrystals were hitherto determined are 160°C for Cu, $D_{Cu}(T) = 2.1 \times 10^{-3} \exp[-0.96(eV)/kT]$ [2], 100°C for Ag, $D_{Ag}(T) = 2.6 \times 10^{-5} \exp[-0.75(eV)/kT]$ [3]; and 500°C for gold, $D_{Au}(T) = 91 \exp(-2.1(eV)/kT)$ [4]. To explain such extremely high diffusivities it is believed that FDs move through CdS as interstitials. However, since the in-diffusion of any of FD transforms n-type CdS into a highly compensated material [1–4], the effective electrical action of Cu, Ag or Au in CdS is clearly acceptor like. To clarify these controversies, we have monitored changes of electrical properties of CdS crystals due to in-diffusion of a particular fast diffusor (by $C-V$), in parallel with changes occurring at the microscopic level (by PAC). From the correlation between microscopic and macroscopic data it was possible to propose some compensation mechanisms (or exclude some others) by which FDs change the electrical properties of CdS.

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2. Experimental details and methodology

2.1. Influence of FD in-diffusion on the electrical properties

The dynamics of the low- T in-diffusion was quantitatively determined by C - V measurements. The penetrating FD atoms compensate donors in n-CdS and therefore change the sample capacitance. A capacitor structure was created in which one 'plate' (and one contact) was the evaporated FD dot, while the other 'plate' was the rest of still conductive n-CdS, with alloyed In as a second contact. The typical area, A , of the dot was 10–20 mm². By measuring the capacitance $C = \epsilon A/W$, the thickness of the SI-layer, W , reflecting the penetration of FD, was determined after each annealing step at temperature T_a . Furthermore, the C - V measurement enabled the profiling of effective, uncompensated, donor concentrations, $n = N_{D,eff.} \equiv N_D - N_A = 2/[(qA^2\epsilon)d(1/C^2)/dV]$. By measuring $C(V)$ at various T_a as a function of time, the penetration rate, and then diffusion coefficients, of each FD could be determined with great precision and spatial resolution from

$$N_{FD}(x) = N_{FD}(0)\text{erfc}[x/2(Dt)^{1/2}], \quad (1)$$

where $N_{FD}(0)$ is the concentration of dopants at the surface, $N_{FD}(x)$ the concentration of FD at depth x , diffused for time t at chosen T_a and diffusion coefficient $D(T_a)$. Measurements were done for Cu and Au, whereas for Ag the low- T diffusion data already exist [3].

Changes at the atomic level due to in-diffusion of FD

The perturbed $\gamma\gamma$ angular correlation (PAC) spectroscopy is a nuclear hyperfine technique which gives detailed and quantitative information about the immediate surrounding of the probe atom [5]. From the fit of a PAC spectrum $R(t)$, one can determine characteristic PAC parameters: the hyperfine interaction strength, ν_Q , and the asymmetry parameter η of the local electric field gradient (EFG). Each PAC 'signature' (ν_Q and η) unambiguously labels a particular probe-atom-defect configuration, allowing its easy qualitative and quantitative identification. The CdS samples were first pre-doped with very small amount ($\approx 10^{11}$ cm⁻³) of radioactive ¹¹¹In probe atoms by diffusion at 800°C for 90 min under 2 atm vapor pressure of sulfur. Practically, all probe atoms were embedded within 1.5 μ m from the surface (40% within first 0.2 μ m), as determined by gradual etching. Two types of pre-doped samples were prepared: (a) Samples in which all ¹¹¹In atoms were incorporated at Cd donor-sites (In_{Cd}^+) [6], resulting in a single, 7.4 MHz frequency in PAC spectra (Fig. 4c, Site 1). (b) Samples in which about half of ¹¹¹In was incorporated as In_{Cd} , while the other half was paired with Cd vacancies,

($\text{In}_{Cd}^+ - \text{V}_{Cd}^{2-}$), characterized by the 72.4 and 78.7 MHz frequencies [6] (Site 2 and 3, respectively). The ($\text{In}_{Cd}^+ - \text{V}_{Cd}^{2-}$) pairs are acceptors, and hence pose a potential trap for any diffusing donors. On both types of samples a FD layer was evaporated. Annealing was performed either under S or Cd partial pressure, in the temperature interval from RT up to 700°C. After each annealing step a PAC spectrum was recorded.

3. Results and discussion

3.1. Influence of the FD in-diffusion on electrical properties

A gamut of C - V spectra measured on CdS:Cu annealed for up to 109 h at $T_a = 100^\circ\text{C}$ is shown in Fig. 1. At first, while the barrier is building up, the maximum of C only shifts away from the $V = 0$ position. Once the barrier has been formed, further annealing reduces C as the acceptors penetrate deeper into the CdS and the thickness of SI layer increases. The resulting decrease of the uncompensated donor concentration and the shifting of the penetration depth W is depicted in Fig. 2. Eq. (1) then enables the calculation of the penetration rate $N_{Cu}(x)/N_{Cu}(0)$ and the diffusion coefficient $D_{Cu}(100)$.

All results are summarized in Fig. 3. Full lines represent results from the present study while dotted lines are calculated from Refs. [2–4] including data for the lowest reported T_a . It can be seen that Cu was found to be the fastest diffusing for all also in the low T_a range, followed by Ag and Au. From the standpoint of the influence of FD on electrical properties, the most important fact is that all of the studied FD's in CdS act effectively as acceptors causing a complete compensation of donors ($N_{D,eff}$ in the 10^{15} – 10^{16} /cm³ range) in the surface region of n-CdS.

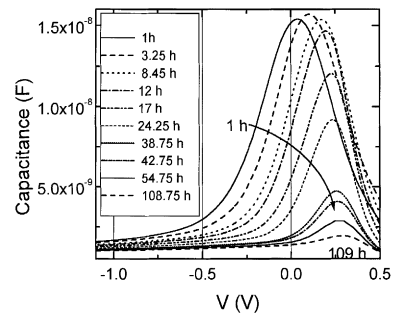


Fig. 1. A series of C - V spectra of CdS:Cu annealed at 100°C from 1 up to 108.75 h. For each curve the corresponding annealing time is given in the figure.

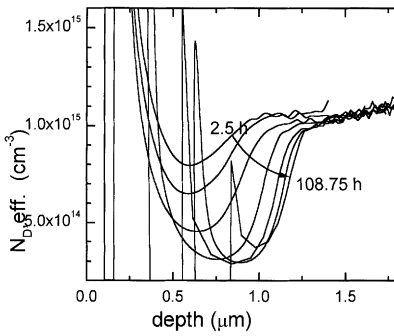


Fig. 2. Spatial distribution of the uncompensated donors concentration $N_{D,eff}$, for CdS:Cu sample annealed at 100°C for various annealing time, t_a , indicated in the figure. For larger t_a the penetration depth $W(t_a, T_a)$, and the whole profile of $N_{D,eff}(x)$, shifts deeper into the crystal.

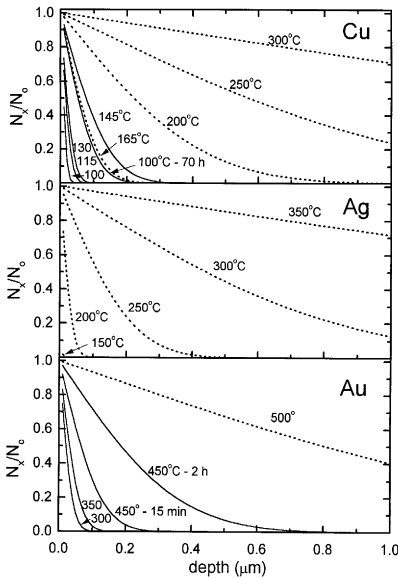


Fig. 3. Penetration rate $N_{FD}(x)/N_{FD}(0)$ for Cu, Ag, and Au diffusion in CdS, calculated from Eq. (1) with low- T values of diffusion coefficients obtained for Cu and Au from this work (full line), while D_{Ag} was taken from Ref. [2] (dashed line). For a comparison, lowest previously reported penetration rates for Cu are calculated from Ref. [2] and for Au from Ref. [4] (dashed). The diffusion time, t_a was 30 min, except for Cu at 100°C, 115°C and 130°C (2 h) or if indicated otherwise.

3.2. Changes at the atomic level due to in-diffusion of FD

Thermal treatment of CdS:FD brought about considerable changes in the microscopic surrounding of the ^{111}In probe atoms, observed at T_a as low as 145°C in CdS:Cu, at $T_a = 200^\circ\text{C}$ in CdS:Ag and at 450°C

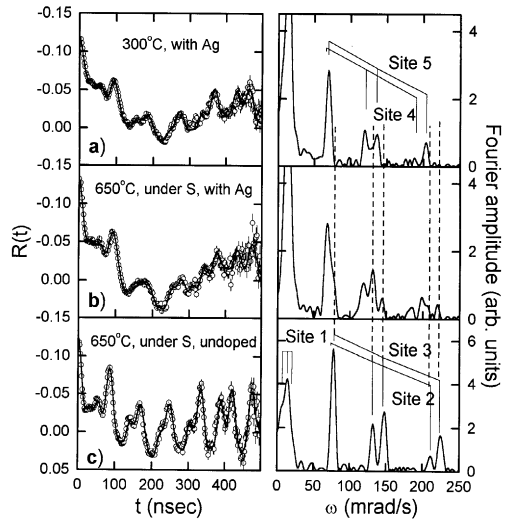


Fig. 4. PAC spectra (left) and their Fourier transforms (right) of a CdS sample pre-doped with ^{111}In probe atoms, after the evaporation of Ag at RT and annealing at indicated temperatures under S pressure (Figs. 4a and b). Spectrum of a sample without Ag is given for comparison (Fig. 4c).

in CdS:Au. In undoped samples (without intentionally added FD) first changes in PAC spectra were observed above 500°C [5,7].

Fig. 4 gives essential points regarding the changes in the surroundings of ^{111}In during in-diffusion of Ag. Prior to Ag evaporation the sample was annealed under Cd pressure to minimize V_{Cd} formation. Upon annealing at 200°C a new PAC signal appeared and already at $T_a = 300^\circ\text{C}$ a considerable fraction (35%) of probe atoms was involved in this configuration. Although the corresponding frequencies: $\nu_Q = 65.5$ MHz, $\eta = 0.30$ (Site 4) and $\nu_Q = 70.5$ and $\eta = 0.21$ (Site 5) are quite close to the values belonging to the ordinary pairs (Sites 2 and 3; Fig. 4c) they are clearly different and distinguishable (compare Fig. 4a and c). If, in addition, ordinary vacancies are created by heating the sample under S pressure above 500°C, a mixture of all 5 sites can be obtained (Fig. 4b).

In CdS:Cu samples the presence of Cu was revealed in several ways: as a new signal, also very similar to that belonging to $(\text{In}_{Cd}-V_{Cd})$ pairs, as an increase of the fraction of $(\text{In}_{Cd}-V_{Cd})$ pairs, and as an additional signal characterized by $\nu_Q = 20$ MHz, $\eta \leq 0.3$, the last one only in samples annealed under Cd pressure. This PAC signal was already observed in diffused CdS:In [6] but was not recognized as related to Cu.

In Au diffused samples no new frequencies were observed. However, vacancies appeared at $T_a = 450^\circ\text{C}$, which is somewhat lower than the temperatures reported

for thermal creation of vacancies in undoped samples [5,7]. Furthermore, once created, V_{Cd} in Au-saturated samples cannot be easily annihilated by annealing under Cd pressure, as it is the case in undoped samples.

3.3. The correlation of microscopic and macroscopic results

By comparison of $C-V$ and PAC results, the connection between microscopic and macroscopic properties in FD-doped CdS crystals could be established. We have found that:

(a) The appearance of new features in the PAC spectra, observed already at low T_a , correlates with the penetration of particular a FD into the 0.1–0.2 μm surface layer. Hence, these PAC features, in all cases, can be safely related to the in-diffusion of FDs.

(b) New configurations, observed in Ag and Cu doped samples, have PAC signatures so similar to those of the $(\text{In}_{Cd}-V_{Cd})$ pairs (Fig. 4) that they have to originate from complexes which contain $(\text{In}_{Cd}-V_{Cd})$. For these complexes we propose a microscopic structure $(\text{In}_{Cd}^+-V_{Cd}^{2-}-\text{FD}_i^+)^0$, in which FD_i (Ag or Cu interstitial) should be 2.5 sites away from the probe atoms. Such assignment agrees with the expectation that the diffusing FD interstitials (Cu_i^+ or Ag_i^+), which are donors, are attracted to the V_{Cd}^{2-} side of the pair whereas, at the same time, repulsed from the In_{Cd}^+ side. This makes the interstitial lattice sites farthest from In_{Cd}^+ energetically most favorable, and the observed small perturbation of the pair frequencies is then understandable. No indication of such complexes was observed in Au doped CdS. Since this complex should be neutral, it represents an efficient mechanism for the compensation of both In_{Cd} and FD_i donors.

(c) In CdS samples with evaporated Au, Cd vacancies were detected (through their pairing with $^{111}\text{In}_{Cd}$) already at 450°C. Taking into account the conclusions (a) and (b), it seems that due to the presence of FDs the V_{Cd} appear at T_a lower than in undoped CdS.

(d) The 20 MHz signal is now positively related to Cu, but its microscopic structure and possible electrical activity is yet to be identified.

(e) The formation of neutral donor–acceptor pairs of the $(\text{In}_{Cd}-\text{FD}_{Cd})$ type was not observed; hence, this is not the mechanism by which the substitutional donors (like $^{111}\text{In}_{Cd}$) in CdS are compensated. Even if one should prove that the 20 MHz PAC signal belongs to $(\text{In}_{Cd}-\text{Cu}_{Cd})$, its fraction never exceeded more than $\frac{1}{3}$ of

In_{Cd} donors, indicating that most donors were compensated in some other way.

4. Conclusions

The presented results suggest a complex microscopic mechanism by which FD in-diffusion creates highly compensated semi-insulating Cds. Although all studied FD atoms act as acceptors, the microscopic mechanisms of compensation are multiple and differ for the different FDs, particularly in the relative importance of these mechanisms. The results are compatible with a notion that the diffusion of FD atoms into CdS provokes simultaneous in-diffusion of Cd vacancies. Some of these vacancies become trapped at donors resulting in a direct electrical passivation. The others create empty sites in the Cd sublattice (otherwise lacking in CdS), enabling the diffusing FD atoms to switch from interstitial donor sites (FD_i) onto substitutional acceptor sites (FD_{Cd}). In Au doped CdS most of the donors are compensated directly by V_{Cd} trapped at the nearest Cd site, whereas in CdS:Ag or CdS:Cu the majority of donors are electrically compensated from the distance, most probably by FD_{Cd} acceptors.

Acknowledgements

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