

Cd-H pairs in GaAs: Identification and stability

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The Cd-H complex in ^{111m}Cd -doped GaAs implanted with low-energy (150–400 eV) hydrogen atoms is identified and studied by perturbed angular correlation spectroscopy using radioactive ^{111m}Cd as a probe. By measuring the fraction of Cd-H pairs in an isochronal annealing experiment, the stability of the pairs is deduced yielding a dissociation energy of $E_D = 1.35(10)$ eV. After ^{111m}Cd implantation but preceding the H loading, the GaAs samples have to be annealed at temperatures exceeding 900 K in order to form Cd-H pairs. These temperatures are in agreement with the temperature range required for electrical activation of Cd implants, suggesting that a Coulombic interaction is responsible for the formation of Cd-H pairs in GaAs.

In recent years the role of hydrogen in semiconductors has created much interest,^{1,2} because of its technological implications; many commonly used processing steps (i.e., plasma or chemical etching) may unintentionally introduce hydrogen into the material and thus alter its electrical characteristics. In GaAs, like in other compound semiconductors, the identification of a unique complex responsible for the passivation by electrical measurements is complicated by deep levels acting concurrently as hydrogen traps, thereby affecting the electrical properties of the material.³ By a combination of electrical and infrared absorption measurements, however, it was shown that the passivation of shallow donors and acceptors in GaAs is accompanied by the formation of dopant-H pairs.^{4–6} The stability of this passivation has so far been investigated only by electrical measurements in combination with depth profiling using either secondary-ion mass spectrometry (SIMS) or $C-V$ techniques.^{4,5} These techniques, however, provide no direct information on the nature of the passivating complex because they are not able to distinguish between different complexes. The dissociation energies deduced from these experiments are about 2.1 eV for donor-H pairs and about 1.6 eV for the only investigated acceptor (Zn)-H pairs.⁵

In the present work information on the nature of complexes formed in Cd-doped GaAs after H-loading is presented. For the identification of the Cd-H pairs the perturbed angular correlation (PAC) technique with ^{111m}Cd as a locally sensitive probe was employed together with low-energy H^+ implantation (150–400 eV), which was used to introduce hydrogen under well-defined conditions. In contrast to H-loading by a plasma, this method minimizes the damage on the lattice and offers control on the amount of H^+ introduced. The formation and stability of the Cd-H pairs in GaAs is studied and a correlation between the electrical activation of Cd as an acceptor in GaAs and the efficiency of pair formation is proposed.

In a PAC experiment, the precession frequencies of a nuclear spin (the 5/2 spin of ^{111m}Cd in the present case), which are induced by electric field gradients arising from nearby defects in the crystal environment are measured. These frequencies are deduced from measurements of the time dependence of the angular correlation between two consecutively emitted γ rays resulting from the nuclear decay of the radioactive probe ^{111m}Cd . A $R(t)$ spectrum is generated from the raw data by taking ratios of counting rates of pairs of different γ -ray detectors. This $R(t)$ spectrum shows a periodic modulation if the probe atom traps a defect such as a hydrogen atom. The associated frequency $\nu_Q = eQV_{zz}/h$ arises from the interaction between the probe's nuclear quadrupole moment Q and the defect specific electric field gradient tensor with its largest principal component V_{zz} . In addition to the defect specific frequency ν_Q , the fraction of probe atoms associated with this defect is directly determined by the amplitude of the modulation in the $R(t)$ spectrum. A more detailed description of the PAC method is given elsewhere.⁷

In the present work undoped, liquid-encapsulated Czochralski-grown $\langle 100 \rangle$ cut GaAs crystals were used. Implantation of the samples with ^{111m}Cd was carried out after proper surface cleaning at the on-line isotope separator ISOLDE at CERN with an energy of 60 keV. The implantation dose was in the range of 10^{12} – 10^{13} cm^{-2} leading to a Cd profile located at a depth of about 25 nm (straggling 11 nm) with a peak concentration of 10^{17} – 10^{18} cm^{-3} . To obtain optimum electrical activation of Cd the following conditions were chosen: Implantation temperature of 473(10) K followed by rapid thermal annealing (RTA) at 1100 K for 20 s under flowing nitrogen gas. These conditions are known to lead to electrical activation of implants in GaAs.⁸ A face-to-face GaAs proximity cap, pressed to the sample by a Mo clamp, was used to minimize surface degradation. The implanted and annealed

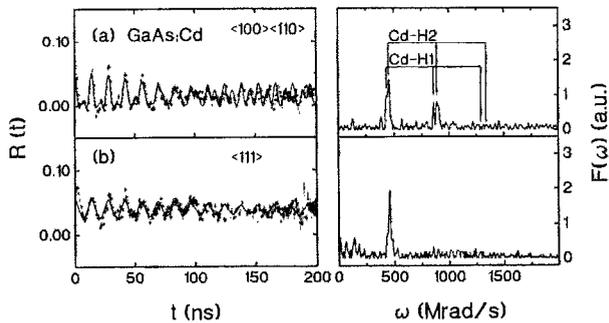


FIG. 1. $R(t)$ spectra (left) and their corresponding Fourier spectra (right) of GaAs doped with ^{111m}Cd , annealed (RTA) at 1073 K for 20 s and subsequently implanted with 400 eV H^+ to a dose of 10^{15} cm^{-2} . The spectra, measured at 300 K with detectors along $\langle 100 \rangle$ $\langle 110 \rangle$ (a) and along $\langle 111 \rangle$ lattice directions (b), show two $\langle 111 \rangle$ axially symmetric field gradients Cd-H1 ($\nu_Q = 457 \text{ MHz}$) and Cd-H2 ($\nu_Q = 481 \text{ MHz}$).

samples were loaded with H^+ by using a low-energy implanter that provides a mass separated H^+ beam. Energies in the range from 150 to 400 eV and doses up to 10^{16} cm^{-2} were employed. The PAC measurements were performed at 300 K using eight or four detector setups.

$R(t)$ spectra and their corresponding Fourier transforms $F(\omega)$, measured at ^{111m}Cd -doped samples implanted with 400 eV H^+ to a dose of 10^{15} cm^{-2} , are displayed in Fig. 1 (left and right, respectively). The upper part [Fig. 1(a)] shows a spectrum recorded with γ detectors placed along $\langle 100 \rangle$ and $\langle 110 \rangle$ lattice directions, while the lower one [Fig. 1(b)] was taken with the detectors set along the $\langle 111 \rangle$ directions of the same GaAs sample. Both $R(t)$ spectra show a modulation typical for the presence of a defect next to the ^{111m}Cd probe atom. The amplitude of the modulation yields 30% of the Cd atoms to be associated with this defect. The Fourier transform $F(\omega)$ of the upper $R(t)$ spectrum [Fig. 1(a)] exhibits two frequency triplets denoted by Cd-H1 and Cd-H2, revealing that actually two different complexes are formed with two slightly different defect specific frequencies of $\nu_Q = 457(2) \text{ MHz}$ (Cd-H1) and $481(2) \text{ MHz}$ (Cd-H2). The frequency ratio within each triplet is indicative of the axial symmetry of the complexes. The vanishing of the two higher Fourier components in the measurement with detectors along $\langle 111 \rangle$ directions [Fig. 1(b)] proves that the observed axially symmetric complexes are parallel to $\langle 111 \rangle$ axes of the GaAs lattice. In this Fourier spectrum the two frequencies belonging to Cd-H1 and Cd-H2, respectively, are still present but are unresolved as evidenced by the broadening of the Fourier peak and by the damping of the $R(t)$ spectrum. The fact that H^+ implantations down to energies as low as 150 eV always produce the same frequencies proves that the complexes are not damage related but are caused by hydrogen located in the vicinity of the probe atom. The possibility that the observed complexes are caused by a lattice defect arising from the H^+ implantation is excluded because a 150 eV hydrogen atom transfers a maximum kinetic energy of 8 eV to a lattice atom, an energy which is not sufficient for the displacement of either a Ga or an As atom. Therefore, it is concluded that the formed Cd-H

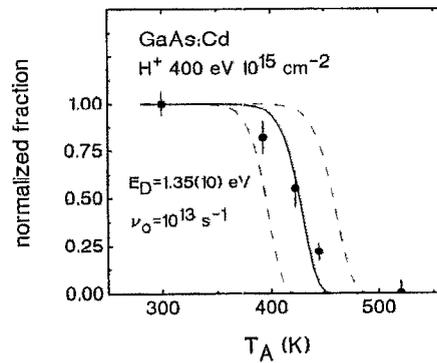


FIG. 2. Fractions of Cd-H pairs after annealing at different temperatures for 10 min in air, normalized to the fraction of Cd-H pairs observed in the same sample without annealing. The full line corresponds to the best fit assuming a single step dissociation process with the dissociation energy $E_D = 1.35 \text{ eV}$ and the attempt frequency of 10^{13} s^{-1} . The two dashed lines correspond to $E_D = 1.25$ and $E_D = 1.45 \text{ eV}$.

complexes are axially symmetric arranged along $\langle 111 \rangle$ lattice directions. The identification of the observed frequencies with Cd-H complexes is supported by low-energy implantations of 150 eV Ar with comparable doses which gives rise to only a very small fraction of Cd-H pairs (less than 5%); these small amounts can be accounted for by elastic recoil implantation of hydrogen from surface H_2O /hydrocarbon contaminants, as well known for the case of Si.^{9,10} Furthermore, the same frequencies have been observed by Baurichter *et al.* in a PAC experiment on ^{111m}Cd -doped GaAs that was exposed to a hydrogen plasma.^{11,12} Because plasma-induced damage could not be excluded, an unambiguous identification of the frequencies with Cd-H complexes was not possible in that work. The fact that the presently observed complexes are oriented along a $\langle 111 \rangle$ direction in the GaAs crystal is in agreement with theoretical predictions¹³ and with other experimental results.⁶ Based on preliminary results the occurrence of two different frequencies could reflect either the existence of two different H lattice sites or a number of H atoms in the Cd-H complex. Due to the preferential formation of Cd-H1 at lower H^+ doses ($< 10^{15} \text{ cm}^{-2}$, 150 eV, implantation temperature 350 K) the assignment of Cd-H1 and Cd-H2 to a Cd-H pair and a Cd-H₂ complex, respectively, is suggested. Since the complexes within the experimental uncertainty exhibit the identical dissociation temperature and are both assumed to cause passivation of the acceptor atoms, they will be treated as one, and the data presented in Figs. 2 and 3 correspond to the sum of the amplitudes of Cd-H1 and Cd-H2.

In order to study the stability of the Cd-H pairs, ^{111m}Cd implanted and annealed GaAs samples were hydrogenated by a 400 eV, 10^{15} cm^{-2} H^+ implantation. The short half-life of the probe nucleus ^{111m}Cd (48 min) does not allow the performance of a series of isochronal annealing experiments on the same sample. Therefore, one sample was divided in two for each temperature; one part was used to obtain a PAC reference spectrum and the other was exposed to a low-temperature annealing for 10 min followed by a PAC measurement. Figure 2 shows the

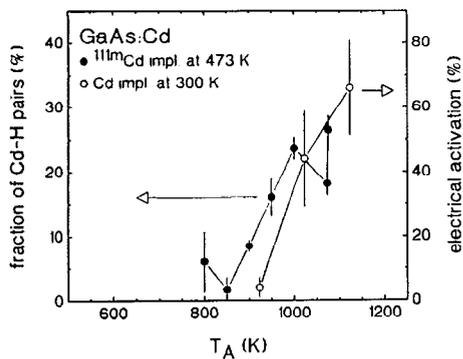


FIG. 3. Fractions of ^{111m}Cd -H pairs formed (full points) after 150 eV H^+ implantation at 300 K with a dose of $2.5 \times 10^{14} \text{ cm}^{-2}$ plotted as a function of rapid thermal annealing temperature following the 60 keV ^{111m}Cd implantation. For comparison the electrical activation of Cd implants (100 keV, 10^{13} cm^{-2}) after 20 min furnace annealing (open points) as extracted from Fig. 1 in Ref. 8 is shown.

Cd-H fraction normalized to the fraction measured in the corresponding reference sample for different annealing temperatures. It is evident from Fig. 2 that heating the sample to about 450 K leads to the complete dissociation of all Cd-H pairs. The temperature dependence shown in Fig. 2 can be roughly reproduced by calculations assuming a single step dissociation process and an attempt frequency of 10^{13} s^{-1} . The solid line in Fig. 2 corresponds to the best fit yielding a dissociation energy $E_D = 1.35(10) \text{ eV}$. The fairly low activation energy found here is in agreement with a similarly low activation energy of $E_D = 1.6 \text{ eV}$ measured for the acceptor Zn paired with hydrogen in GaAs.⁵ The fact that the calculated curve does not exactly follow the experimental data reflects the experimental uncertainty of the plotted Cd-H fractions, which is caused by the use of different samples for each annealing step.

The trapping of positive¹⁴ or neutral⁴ hydrogen at negatively charged acceptors is believed to be the formation mechanism for the passivating complex. Therefore the electrical activation of the acceptor seems to be essential for the formation of acceptor-H pairs. To verify this point the following study was undertaken: ^{111m}Cd was implanted at 473 K into different GaAs samples. Each sample was subsequently annealed (RTA) at a different temperature covering the temperature range between 800 and 1100 K. This range includes temperatures at which the electrical

activation of implants in GaAs is known to occur.⁸ Following this annealing, all samples were exposed to a 150 eV H^+ implantation at 300 K with a dose of $2.4 \times 10^{14} \text{ cm}^{-2}$. Figure 3 shows the fraction of Cd-H pairs measured for these samples. The increase of the Cd-H fraction as a function of annealing temperature is obvious. For comparison the results of the electrical activation of implanted Cd in GaAs which are extracted from Fig. 1 in Ref. 8, are also plotted in Fig. 3; here, GaAs was implanted at 300 K with 100 keV Cd ions (10^{13} cm^{-2}) and subsequently furnace annealed for 20 min. The increase of the electrical activation of the acceptor Cd just parallels the increase of the formation of Cd-H pairs. It is, therefore, concluded that the electrical activation of the acceptor is essential for the pairing process. A Coulombic interaction between the negatively charged acceptor and the hydrogen is thus the mechanism responsible for the formation of Cd-H pairs in GaAs.

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