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FIRST PAC STUDIES ON THE HYDROGEN DIFFUSION IN III-V SEMICONDUCTORS

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ABSTRACT

We report on first experiments which observe on a microscopic scale the migration of isolated hydrogen in InP, InAs and GaAs. Using the radioactive acceptor ^{117}Cd, Cd-H pairs have been formed in these III-V semiconductors. After the decay of ^{117}Cd to ^{117}In, H is no longer bound to ^{117}In and can diffuse freely. This diffusion has been observed by perturbed $\gamma\gamma$ angular correlation (PAC) spectroscopy. At 10 K, the occupation of two different lattice sites by hydrogen has been observed.

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1 Introduction

During the last ten years, the behavior of hydrogen in semiconductors has been extensively studied, mainly focused on the aspects related to the modification of the electronic properties due to the interaction of hydrogen with electrically active centers. The formation of complexes between dopants or other defects can result in an electrical passivation and the annihilation of the corresponding levels in the band gap. Both, for elementary and compound semiconductors, the formation probability, the atomic structure, and the thermal stability of such complexes has been extensively studied by various theoretical and experimental techniques [1,2].

The knowledge on the basic mechanisms of hydrogen diffusion in III-V semiconductors is much less developed. Most of the experimental results available up to now [3] are based on macroscopic techniques like the determination of diffusion profiles of deuterated samples by SIMS or the observation of carrier profiles obtained in hydrogenated samples where the sample is part of a Schottky diode which allows the annealing with an reverse bias applied across the Schottky contact. The interpretation of the data obtained by these techniques is complicated by the different charge states of hydrogen in semiconductors (H^+, H^0, H^-) which are also linked to different equilibrium lattice sites. In addition, the formation probability of these states depends on the position of the Fermi level.

In this paper, we present first results on the direct microscopic observation of single jumps of diffusing isolated hydrogen using the perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC). The idea of the experiment is the formation of acceptor-hydrogen pairs in III-V semiconductors using the radioactive acceptor ^{117}Cd which decays to ^{117}In where the PAC measurement takes place. After this transmutation, the hydrogen is no longer bound by Coulomb attraction to ^{117}In and can diffuse freely. The jumps out of the neighborhood of the ^{117}In atoms can be observed by PAC as function of temperature. Using a different PAC probe atom, similar experiments have been performed to study the diffusion of oxygen in tantalum [4].

2 Experiment

Semi-insulating GaAs, InP, and InAs samples have been implanted with ^{117}Ag using a chemically selective laser ionization ion source [5] at the ISOLDE on-line separator at CERN with an energy of 60 keV and a dose of 2×10^{11} cm^{-2}. The ^{117}Ag decays within minutes to ^{117}Cd with a life-time of about 3 h which further decays to an excited state of ^{117}In where the actual PAC measurement takes place. To remove the implantation induced damage after all ^{117}Ag has decayed to ^{117}Cd, the GaAs and InP samples have been annealed at 1073 K and the

InAs samples at 930 K by furnace annealing in a closed quartz tube for 600 s under As or P atmosphere, respectively.

The hydrogen loading has been performed at 323 K using a mass-separated 100 eV H^+ ion beam and a dose of 3×10^{14} cm^{-2} produced by a low-energy ion implanter. This procedure allows a quantitative control of the introduced amount of H and avoids the unintentional introduction of any other impurity atoms.

After this step, ^{117}Cd-H pairs have been formed and the immediate neighborhood of the ^{117}In atoms and the presence of hydrogen was monitored with the perturbed γγ angular correlation technique (PAC) at 10 K and at 78 K. Here the electric field gradient tensor (EFG) at the site of the radioactive probe atom is measured. The EFG causes a hyperfine splitting of an excited state of ^{117}In created by the γ decay of ^{117}In that is measured by PAC. The EFG is described by the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$ (Q denotes the nuclear quadrupole moment and V_{zz} the largest component of the diagonalized EFG tensor) and the asymmetry parameter η. These values are characteristic for specific defects and the fraction of probe atoms involved in this complex can be determined from the amplitude of the modulation of the PAC spectrum *R(t)* induced by this hyperfine interaction [6]. For the case of ^{117}In, each EFG is described by one frequency in the PAC spectrum.

3 Results and Discussion

Using the radioactive acceptor ^{111m}Cd, the formation of Cd-H pairs in III-V semiconductors has been studied extensively. Therefore the conditions for the passivation of up to 80% off all ^{111m}Cd acceptors, the microscopic structure and the stability of these pairs is well known [7,8]. All these holds also for the chemically identical isotope ^{117}Cd.

In Fig. 1, PAC spectra recorded at 10 K along with their Fourier transforms are shown for InP and GaAs. From the Fourier transforms it is obvious that for both systems and also for InAs (s. Fig. 2 top) two EFG are observed (s. Table 1, the apparent splitting of the higher frequency is probably an artifact of the Fourier transformation.). The observed amplitudes correspond to total fractions of probe atoms observing these configurations of about 30% for InP, 60% for GaAs and 50% for InAs, respectively. Both EFG have to be related to hydrogen in the immediate vicinity of the probe atom ^{117}In. In earlier PAC experiments using the radioactive acceptor ^{111m}Cd, under similar conditions only one Cd-H configuration with a <111> symmetry has been observed [7,8], probably a H atom occupying a 'bond-center' site on a Cd-As or Cd-P bond, respectively. The existence of two EFG observed at ^{117}In can be understood, if one assumes that after the decay of ^{117}Cd the initially bound H relaxes to two different equilibrium lattice positions of isolated interstitial H atoms.

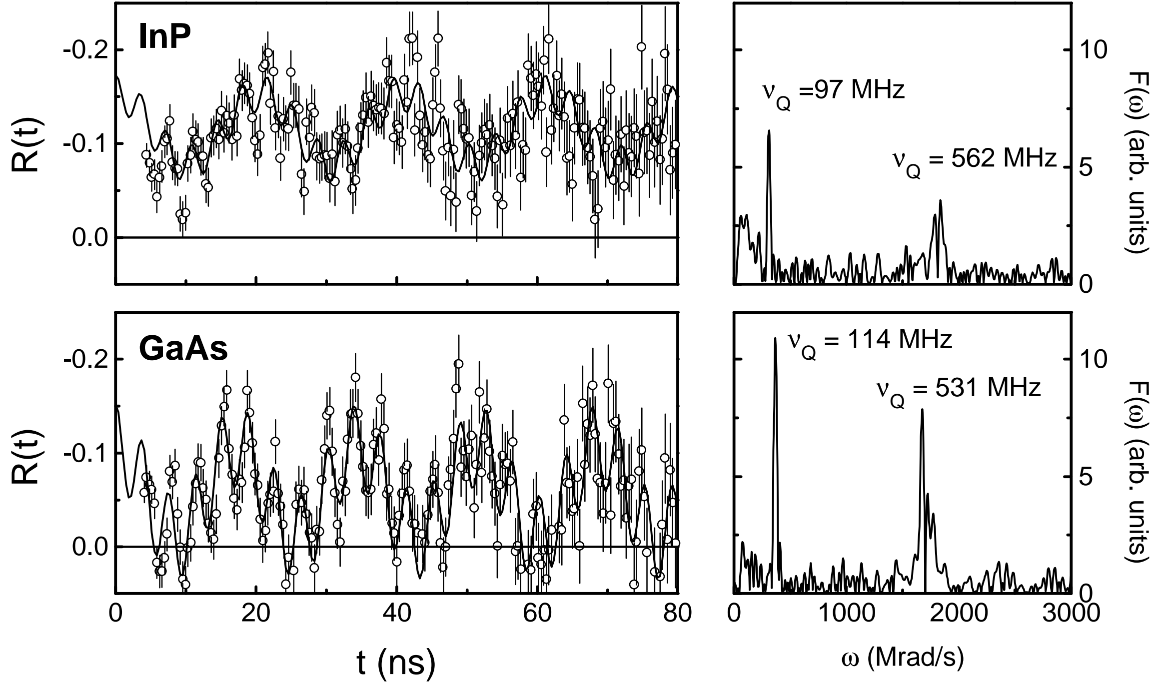

Figure 1: PAC spectra and their Fourier transforms for InP (top) and GaAs (bottom) doped with ^{117}Cd, loaded with H by low energy implantation (100 eV, 3×10^{14} cm^{-2}) at 323 K, and measured at 10 K.

The only microscopical information on isolated H comes from muon spin rotation spectroscopy (μSR) where the muonium acts as a light isotope of hydrogen. For GaAs, two sites of isolated muonium have been observed [9]: A tetrahedral interstitial site with four Ga neighbors ("normal muonium") and a site on a bond bridging two host atoms ("anomalous muonium") with a population probability of the two sites of about 2 to 1. The assignment of these sites is also supported by theoretical calculations of Pavesi and Gianozzi [10]. All of this corresponds perfectly to our PAC results. Moreover, the relaxation of the hydrogen into these sites after the decay of ^{117}Cd has to occur within a few ns because no sign of any dynamical relaxation is observed in the PAC spectra.

Compound	ν_Q (MHz)		
	^{117}In		^{111m}Cd
InAs	99(2)	505(2)	427(1)
GaAs	114(2)	531(2)	457(2)
InP	97(2)	562(3)	484(1)

Table 1: Quadrupole coupling constants ν_Q for ^{117}In-H and ^{111m}Cd-H [7] pairs observed in various III-V semiconductors at 10 K.

Fig. 2 shows two PAC spectra for InAs after H doping recorded at 10 K (top) and at 78 K (bottom). Raising the temperature to 78 K reduces the fraction of ^{117}In atoms observing H atoms from 50% to about 25%. This means, that half of the H atoms originally observed at 10 K have performed enough jumps at 78 K within a few ns so that they cannot longer be observed by the “shortsighted” PAC. They have left the first nearest neighborshells of the possible interstitial lattice sites around the probe atom. No new EFG is observed at 78 K leading to the conclusion, that hydrogen does not occupy any other stable lattice sites that may be unreachable at lower temperatures due to an energy barrier. There is also no hint visible in the PAC spectra for any localized fast transition between different sites, e.g. the tetrahedral and the bond-centered interstitial site.

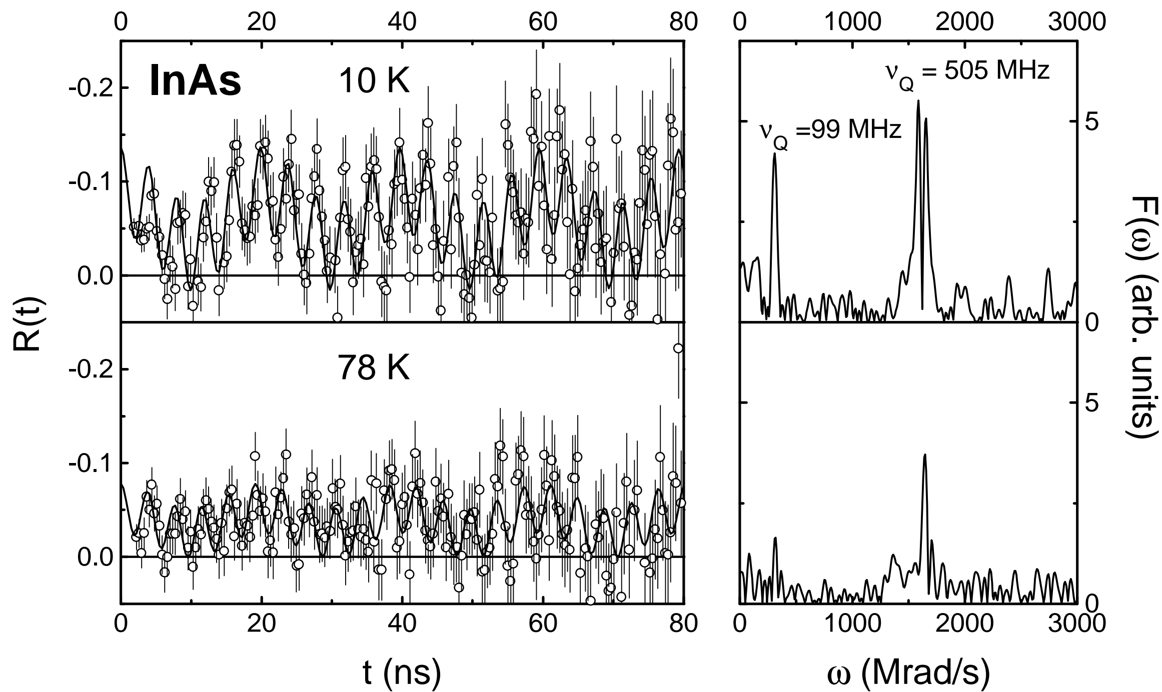

Figure 2: PAC spectra and their Fourier transforms for InAs doped with ^{117}Cd, loaded with H by low energy implantation (100 eV, 3×10^{14} cm^{-2}) at 323 K, and measured at 10 K (top) and 78 K (bottom).

In GaAs, a smaller reduction of the observed fractions has been observed between 10 K and 78 K than in InAs. This indicates a somewhat larger diffusion enthalpy for hydrogen in InAs, but the results available up to now do not allow to estimate any diffusion parameters like diffusion enthalpies or to distinguish between different possible diffusion mechanisms like classical over barrier diffusion or quantum diffusion. The onset of quantum diffusion in GaAs has been observed by μSR at temperatures below 90 K [11].

4 Conclusion

It has been demonstrated, that utilizing the radioactive acceptor ^{117}Cd decaying to ^{117}In for PAC measurements in hydrogenated III-V semiconductors allows the observation of isolated hydrogen states. The first results presented here reveal two distinct interstitial lattice sites occupied by hydrogen at low temperatures in InP, GaAs and InAs. Raising the temperature to 78 K leads to a reduction of the observed fraction which is consistent with the onset of hydrogen diffusion away from the ^{117}In probe atoms. Future investigations as function of the measurement temperature with smaller temperature steps will allow the determination of the diffusion enthalpies for the different hydrogen species. In contrast to macroscopic measurements, the obtained diffusion data should not be influenced by the interaction of the diffusing hydrogen with other charged defects present in the sample. Moreover, by varying the background doping of the used materials, it should be possible to obtain direct information on the influence of the position of the Fermi level on the occurrence of the different hydrogen species and to determine their energy levels within the band gap.

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