ELECTRIC FIELD GRADIENTS OF ACCEPTOR-DONOR PAIRS IN SEMICONDUCTORS

A. Burchard [1], M. Deicher [1], V.N. Fedoseyev [2], D. Forkel-Wirth [3], R. Magerle [1], V.I. Mishin [2], D. Steiner [1], A. Stötzler [1], R. Weissenborn [1], Th. Wichert [4], and the ISOLDE-Collaboration [3]

[1] *Fakultät für Physik, Universität Konstanz, D-78457 Konstanz, Germany*
[2] *Institute of Spectroscopy, 142092 Troitzk, Russia*
[3] *CERN, CH-1211 Geneva 23, Switzerland*
[4] *Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany*

The interaction between substitutional and interstitial donors and single or double acceptors in Si, GaAs, InP, and InAs has been studied by perturbed angular correlation spectroscopy (PAC). For the case of Si, complex formation between ubstitutional donors (As, P) and different radioactive acceptors (^{111}In, ^{111m}Cd, ^{117}Cd) have been observed. The formation of Cd-hydrogen pairs using either ^{111m}Cd or ^{117}Cd are discussed for GaAs, InP, and InAs.

1. Introduction

The formation of pairs and complexes between ionized defects in group IV [1,2], III-V[3] and II-VI semiconductors [4] via Coulombic attraction has been studied extensively by perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC) for more than 10 years. Besides the interest in semiconductor physics on the properties of these complexes like formation probability and thermal stability, the most simple of these defects, pairs between a substitutional dopant (i.e. an acceptor) and one other impurity atom either on a substitutional or interstitial first neighbor lattice site represent model systems to test and enhance theoretical calculations of the electric field gradients (EFG) associated with these pairs. During the last years, due to the availability of fast computers calculations of EFG caused by defects in semiconductors have achieved an astonishing progress [5,6] and may develop to an important tool to identify the structure of defect complexes observed in semiconductors by hyperfine interactions via first principle calculations and to gain more information on these defects not directly accessible by hyperfine interaction techniques, like the lattice relaxation of the defects involved in such complexes or the charge state of the complex. The ISOLDE on-line separator at CERN is able to deliver a range of radioactive probe atoms suitable for PAC which can be used to form such pairs between a specific defect and different probe atoms. The intention of this paper is to present a set of data which hopefully triggers the further development of theoretical calculations of electric field gradients due to simple defect complexes in semiconductors.

In this paper, we will summarize known and present new results of PAC experiments for the formation of different acceptor-donor complexes in Si and the III-V semiconductors GaAs, InP, and InAs. This complex formation has been observed using different PAC probe atoms: ^{111}In/^{111}Cd, ^{111m}Cd, and ^{117}Cd/^{117}In. In Si, the known formation of complexes between the single acceptor ^{111}In (decaying to ^{111}Cd) and the double acceptor ^{111m}Cd and the substitutional donors P and As has been extended to the double acceptor ^{117}Cd decaying to ^{117}In. In the III-V semiconductors, the results of the formation of Cd-H pairs will be presented using either ^{111m}Cd or ^{117}Cd single acceptors. Due to the decay of ^{117}Cd to ^{117}In where the actual PAC measurement takes place, the originally trapped hydrogen is now observed without any Coulombic binding in the neighborhood of the probe atom.

2. Experimental Details

FZ Si doped with P (3×10^{18} cm^{-3} – 2×10^{20} cm^{-3}) and As (2×10^{19} cm^{-3} – 1×10^{20} cm^{-3}) either homogeneously or by ion implantation has been implanted with ^{111}In single acceptors (E = 350 keV, 2×10^{12} cm^{-2}) at the Konstanz implanter. ^{111}In ($T_{1/2}$ = 2.8 d) decays to an excited state of ^{111}Cd where a spin 5/2 intermediate state with 84 ns half-life is used for PAC spectroscopy. The doping with double acceptors has been achieved by implantation of ^{111m}Cd using a plasma ion source or ^{117}Ag using a chemically selective laser ionization ion source [7] at the ISOLDE on-line separator at CERN with an energy of 60 keV and a dose of 2 - 6×10^{11} cm^{-2}. ^{111m}Cd decays with an half-life of 49 min via the same intermediate spin 5/2 state as

^{111}In/^{111}Cd and there is no elemental transmutation involved. The ^{117}Ag decays within minutes to ^{117}Cd with a half-life of about 3 h which further decays to an excited state of ^{117}In where the actual PAC measurement takes place using a state with spin 3/2 and 53.6 ns half-life. The formation of the acceptor-donor complexes in Si has been achieved either by annealing at 900 K for 10 min using a furnace or for 20 s using a rapid thermal annealing setup. Semi-insulating GaAs, InP, and InAs have been implanted with ^{111m}Cd and ^{117}Cd in a similar way as described above. 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 or 373 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.

The immediate neighborhood of the implanted ^{111}In, ^{111m}Cd, and ^{117}Cd and their interactions with donor-like defects was monitored by perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC). Here the electric field gradient tensor (EFG) at the site of the radioactive probe atom is measured. The EFG is described by the quadrupole coupling constant ν_Q and the asymmetry parameter η. These values are characteristic for specific defects nearby the radioactive probe atom and the symmetry of a formed probe-atom-defect complex, its orientation within the lattice, and the fraction of probe atoms involved in this complex can be determined [8]. For the case of ^{117}In, due to the spin 3/2 of the nuclear state used by PAC, only ν_Q and neither η nor the orientation of the EFG can easily be determined.

3. Results and Discussion

Silicon

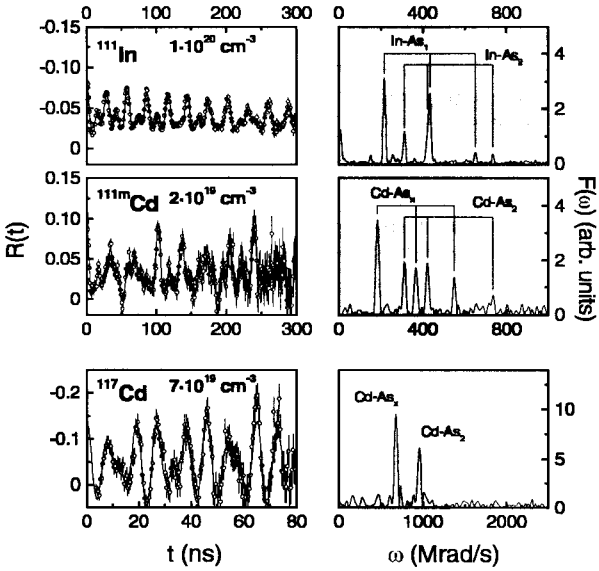

Fig. 1: *PAC spectra (left) and Fourier transforms (right) of acceptor-donor complexes in As (2×10^{19} cm^{-3} – 1×10^{20} cm^{-3}) doped Si using ^{111}In, ^{111m}Cd, and ^{117}Cd as probe atoms.*

Fig. 1 (left) shows the PAC spectra obtained after implanting ^{111}In, ^{111m}Cd, and ^{117}Cd into As doped Si and annealing at 900 K. For all probe atoms the formation of In-donor or Cd-donor complexes can be observed. For the case of ^{111}In (Fig.1 top), complexes involving one As donor (In-As$_1$) and two As donors (In-As$_2$) are created. The identification of these complexes has been established by varying the As concentration and the annealing time [9]. One has to keep in mind that the complexes are formed at the single acceptor ^{111}In but are observed at the double acceptor ^{111}Cd. Using ^{111m}Cd (Fig.1 middle) this transmutation is avoided. In contrast to ^{111}In, a third complex (Cd-As$_x$) is formed which has hyperfine parameters close to In-As$_1$ with a slightly smaller EFG (s. Table I). The other observed complexes are identical to the ones formed at ^{111}In. This third complex is obviously caused by the complex formation at the double acceptor Cd which is, in contrast to In, not compensated by the binding of one single donor. The assignment of Cd-As$_x$ to a trapped single As in a relaxed configuration or to a highly symmetric complex formed by three As donors is still controversial and theory may help to clarify this question. The lower panel of Fig. 1 shows the results for complexes formed at ^{117}Cd but measured at ^{117}In. Once more two different complexes are observed (s. Table I). The assignment of these two complexes to Cd-As$_x$ and Cd-As$_2$, respectively, is at the moment only based on the relative strength of the EFG and the formation probability compared to ^{111m}Cd. But the electrical situation is now different: In contrast to ^{111m}Cd, at the moment of the PAC measurement the ^{117}In-As pair should be a

neutral defect and the complex involving a second As should be of donor-like character. For P doped Si a very similar behavior for all used probe atoms has been found (s. Table I).

Table I: *PAC parameters (nQ, h) and orientation (<ijk>) of acceptor-As and acceptor-P complexes in Si using different radioactive acceptors.*

System (acceptor)	$A\text{-}D_1$			$A\text{-}D_2$			$A\text{-}D_x$		
	ν_Q (Mhz)	η	<ijk>	ν_Q (Mhz)	η	<ijk>	ν_Q (MHz)	η	<ijk>
Si:As									
^{111}In	229	0	<111>	237	0.65				
^{111m}Cd	229	0	<111>	237	0.65		193	0	<111>
^{117}Cd				306(4)			217(4)		
Si:P									
^{111}In	179	0	<111>	195	0.65				
^{11m}Cd	179	0	<111>	195	0.65		165	0	<111>
^{117}Cd				283(4)			204(4)		

III-V Semiconductors

Fig. 2 (left) shows PAC spectra along with their Fourier transforms for GaAs, InP, and InAs doped with ^{111m}Cd and loaded with hydrogen by low energy (100 eV, 3×10^{14} cm^{-2}) implantation. Under this conditions hydrogen forms pairs with up to 80% of all ^{111m}Cd acceptors [3]. For all systems, these pairs are characterized by an axially symmetric EFG ($\eta = 0$) and are oriented along <111> lattice directions. Table II lists the respective PAC parameters ν_Q. These results are consistent with the generally accepted model proposed by Pajot [10] that the hydrogen breaks a Cd-As or Cd-P bond, respectively, saturates the dangling bond, and the free hole annihilates the Cd dangling bond ("bond-center site"). This results in a relaxation of the acceptor and the As or P along a <111> direction but the trigonal symmetry remains conserved as confirmed by the axially symmetric EFG. But without supporting theoretical calculations, PAC spectroscopy can not distinguish between different possible lattice sites of the hydrogen which also preserve the observed <111> symmetry of the EFG.

Even more simple, from a theoretical point of view, is the situation if the Cd-H pairs are formed using ^{117}Cd. After the transmutation of ^{117}Cd to ^{117}In, a group III element, the hydro-

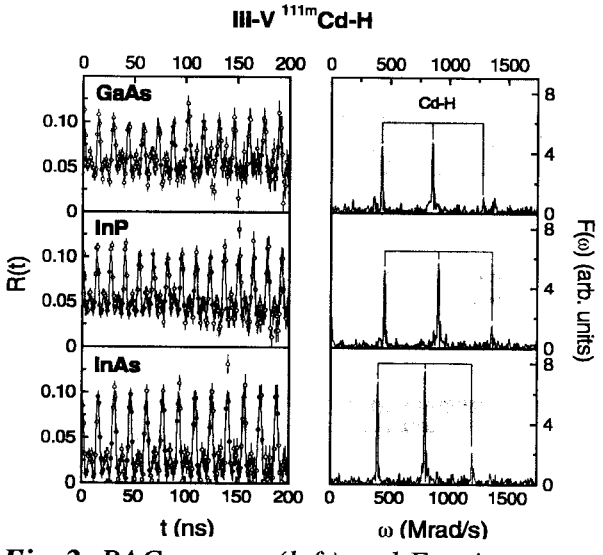

Fig. 2: PAC spectra (left) and Fourier transforms (right) of Cd-H pairs in III-V semiconductors using ^{111m}Cd.

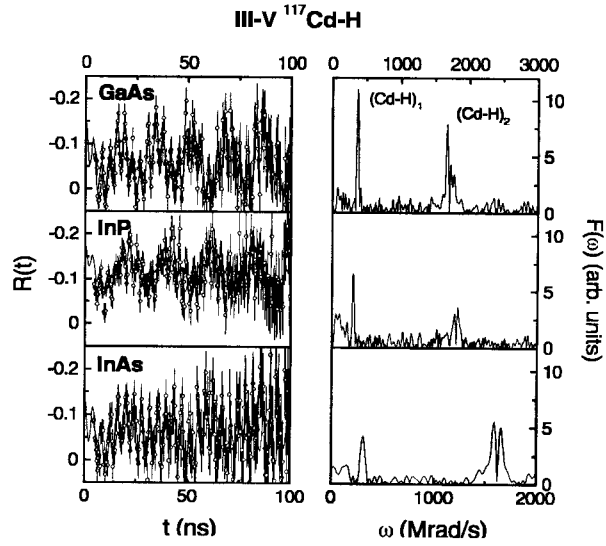

Fig. 3: PAC spectra (left) and Fourier transforms (right) of Cd-H pairs in III-V semiconductors using ^{117}Cd.

gen is no longer bound by Coulomb attraction to ^{117}In. It has been shown, that by observing the probability for jumping of hydrogen out of the neighborhood of ^{117}In can be used to determine the hydrogen diffusion in III-V semiconductors on a microscopical scale [11]. Fig. 3 (left) shows PAC spectra for GaAs, InP, and InAs doped with ^{117}Cd and analogously loaded with hydrogen as in the case of ^{111m}Cd. To avoid any hydrogen diffusion, all measurements have been recorded at 10 K. As can be clearly seen in the corresponding Fourier transforms (Fig. 3 right), all the studied systems show two EFG (s. Table II) belonging to two different interstitial lattice sites of the hydrogen adjacent to ^{117}In. Both EFG have to be related to hydrogen in the immediate vicinity of the probe atom ^{117}In. In PAC experiments using the radioactive acceptor ^{111m}Cd, under similar conditions only one Cd-H configuration with a <111> symmetry is formed. 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. 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 [12]: 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 [13].

Table II: *Quadrupole coupling constants ν_Q for ^{117}Cd-H and ^{111m}Cd-H [3] pairs observed in various III-V semiconductors at 10 K.*

Compound	ν_Q (MHz)		
	^{117}Cd		^{111m}Cd
GaAs	111(2)	515(2)	457(2)
InP	94(2)	549(3)	484(1)
InAs	99(2)	505(2)	427(1)

This work was financially supported by the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie under Grant No. 03-DE5KO1-6.

References

[1] Th. Wichert, M. Deicher, G. Grübel, R. Keller, N. Schulz, and H. Skudlik, Appl. Phys. A 48 (1989) 59.
[2] D. Forkel, N. Achtziger, A. Baurichter, M. Deicher, S. Deubler, M. Puschmann, H. Wolf, and W. Witthuhn, Nucl. Instr. Meth. B 63 (1992) 217.
[3] M. Deicher and W. Pfeiffer, in *Hydrogen in Compound Semiconductors*, ed. S.J. Pearton (Materials Science Forum Vol. 148-149, Trans Tech Publications, Aedermannsdorf, 1994).p. 481.
[4] V. Ostheimer, A. Jost, T. Filz, St. Lauer, H. Wolf, and Th. Wichert, Appl. Phys. Lett. 69 (1996) 2840.
[5] P. Blaha, P. Dufek, K. Schwarz, and H. Haas, Hyp. Int. 97/98 (1996) 3.
[6] A. Settels and P.H. Dederichs, private communication.
[7] V.I. Mishin, V.N. Fedoseyev, H.-J. Kluge, V.S. Letokhov, H.L. Ravn, F. Scheerer, Y. Shirakabe, S. Sundell, and O. Tengblad, Nucl. Instr. Methods B 73 (1993) 550.
[8] Th. Wichert, N. Achtziger, H. Metzner, and R. Sielemann, in *Hyperfine Interactions of Defects in Semiconductors*, ed. G. Langouche (Elsevier, Amsterdam 1992) p. 77.
[9] Th. Wichert and M.L. Swanson, J. Appl. Phys. 66 (1989) 3026.
[10] B. Pajot, Inst. of Phys. Conf. Ser. 95 (1989) 437.
[11] A. Burchard, M. Deicher, R. Magerle, A. Egenter, R. Spengler, and D. Forkel-Wirth, in *Shallow-Level Centers in Semiconductors* ed. by C.A.J. Ammerlaan and B. Pajot (World Scientific, Singapore, 1997) p. 185.
[12] R.F. Kiefl, J.W. Schneider, H. Keller, W. Kündig, W. Odermatt, B.D. Patterson, K.W. Blezey, T.L. Estle, and S.L. Rudaz, Phys. Rev. B 32 (1985) 530.
[13] L. Pavesi and P. Gianozzi, Phys. Rev. B 46 (1992) 4621.