# SOLID STATE PHYSICS WITH RADIOACTIVE ISOTOPES\*

## DORIS FORKEL-WIRTH

#### CERN/TIS, CH-1211 Geneva 23, Switzerland

#### (Received January 8, 1999)

Solid state physics with radioactive atoms employs nuclear techniques like Mößbauer Spectroscopy, Perturbed Angular Correlation,  $\beta$ -NMR and Emission Channeling as well as tracer techniques like Radiotracer Diffusion or radioactive Deep-Level Transient Spectroscopy, Capacitance-Voltage measurements, Hall-effect measurements or Photoluminescence Spectroscopy. Different problems are attacked in metals, semiconductors and superconductors, while defects and impurities in semiconductors still represent the main field of activities. Several possibilities exist to dope samples with radioactive isotopes, ranging from diffusing commercially available radioisotopes such as <sup>111</sup>In into the host lattice up to on-line implantations at ISOLDE/CERN. The paper will give some examples for different types of experiments.

PACS numbers: 61.72.Tt, 61.72.Vv, 71.55.Cn, 71.55.Eq

#### 1. Introduction

Solid state physics with radioactive isotopes represents a wide field, comprising studies of defects and impurities in metals, semiconductors and superconductors. Bulk as well as surface and interface properties of solids are subject of numerous experiments with radioactive isotopes and the number of experimental groups working on these topics has considerably increased during the last years. This augmenting interest is mainly related to two reasons. In the early eighties the application of nuclear techniques like Mößbauer Spectroscopy (MS), Perturbed Angular Correlation (PAC),  $\beta$ -NMR and Emission Channelling (EC) was swapped from metals to semiconductors. Already the first results obtained by the different methods proved the big potential of new information on internal crystal fields, on lattice sites,

<sup>\*</sup> Presented at the International Conference "Nuclear Physics Close to the Barrier", Warszawa, Poland, June 30–July 4, 1998.

on diffusion mechanisms and on the interaction between impurities or impurities and defects in semiconductors. A second boost for solid state physics with radioactive isotopes was experienced in the beginning of the nineties when traditional, non-radioactive semiconductor techniques like Hall effect measurements (HE), Deep Level Transient Spectroscopy (DLTS), Capacitance Voltage Measurements (CV) or Photoluminescence Spectroscopy (PL) were combined with radioactive isotopes. Immediately, this combination proved to be a very successful one.

The nuclear techniques (ME, PAC,  $\beta$ -NMR, EC) are based on the detection of the decay products ( $\alpha$ -particles,  $\beta$ -particles,  $\gamma$ -quanta) emitted by specific, radioactive probe atoms. The spectroscopy techniques of ME, PAC and  $\beta$ -NMR exploit the fact that the emitted particles or quanta carry information about the hyperfine interaction between the electric or magnetic nuclear moments of the specific probe nucleus and the magnetic fields or the electric field gradients of its surroundings. These internal magnetic crystal fields or electric field gradients inform about lattice sites of impurities, the diffusion of impurities and the interaction of impurities or of impurities and defects. Emission Channeling represents a straightforward technique to determine the lattice sites of radioactive probe atoms in crystals. Substitutional or interstitial lattice sites of the probe atoms are identified by counting the emitted  $\alpha$ - or  $\beta$ -particles under different angles with respect to the lattice directions of a single crystal. The sensitivity of EC with respect to the impurity concentration is at least two orders of magnitude higher than that of related ion beam channeling techniques like Rutherford Back Scattering (RBS). A detailed description of all the nuclear techniques is given in reference [1].

The new tracer techniques like radioactive DLTS, CV, HE or PL make use of the chemical transmutation involved in a  $\beta$ -decay. No radioactive decay product is detected, but simply the electrical or optical measurements are periodically repeated over a time interval adapted to the half life of the radioactive impurity under investigation. The intensity of the electrical or optical signals will change in time: these correlated to the parent isotope will decrease and those correlated to the daughter increase. In case the time development of the signal intensities matches the half life of the radioactive probe atom, the chemical nature of the impurity can be unambiguously assigned to the observed electrical or optical properties. Using the radioactive decay constant as a fingerprint of the impurity under study is the obvious advantage of the tracer techniques compared to the corresponding, nonradioactive versions. The basics of the nuclear and the tracer techniques are shortly described in reference [2].

Up to now approximately 100 different radioactive isotopes have been used in solid state physics, ranging from  $^{8}$ Li to  $^{213}$ Fr. They are produced

by nuclear reactions in reactors or at accelerators and the doping of the host lattice is performed either by nuclear reaction inside the material, by recoil implantation or by diffusion or implantation after nuclear production and chemical separation. The radioactive nuclei are used as probes of their structural or electronic environment in metals, insulators, semiconductors or superconductors, on surfaces and interfaces. The major part of the activity is focused on the investigation of defects and impurities in semiconductors such as Si, Ge, III-V or II-VI compounds. The progress in this field is reviewed in several, recent publications [2–8]

## 2. Experimental requirements

## 2.1. Radioactive probe atoms

The choice of a radioactive probe atom for a specific experiment is on one hand determined by its chemical nature and on the other hand by its nuclear properties. Depending on the research subject the probe atom has to represent either a self-atom or an impurity in the host lattice, a property which is governed by its chemical nature. The requirements with respect to the nuclear features depend on the applied technique. The hyperfine methods like MS or PAC are rather limited in the choice of suitable probe atoms since they depend on very specific decay patterns of the probe nuclei. EC and the tracer techniques enjoy a larger choice of suitable isotopes since they just require an  $\alpha$ - or  $\beta$ -decay. As a common feature of all techniques the range of feasible experiments is governed by the half live of the probe atom or its parent isotope, respectively.

Half lives in the order of days are often preferred, since they permit laboratory experiments studying systematically one sample in function of different parameters like annealing conditions, measuring temperature or external pressure. In addition, post-treatments are possible like electron or proton irradiation of the samples for defect studies or the application of Schottky contacts to study semiconductors under different electronic conditions.

Half lives in the order of hours need a reactor, accelerator or an on-line mass separator close by to provide probe atoms during the experiment on a regular basis with a repetition rate of some few hours. The possibilities for the sample treatment are limited, but a wider choice of suitable and interesting probe atoms is available.

Half lives of less than some ten minutes require on-line experiments, *i.e.* the experimental set-up of MS, PAC, EC or  $\beta$ -NMR is directly connected to an accelerator or an on-line mass separator. The probe atoms are repetitively or continuously implanted into the samples. The choice of probe atoms is even more enlarged but for the price of very limited possibilities concerning the subsequent sample treatment.

# 2.2. Doping procedures

The radioactive isotopes are produced at reactors or accelerators. Some combinations of probe atoms and host lattices can be directly achieved by nuclear reactions inside the material under study. Typical examples are the doping of Cadmium and Cadmium compounds with <sup>111</sup>In via the  $^{111}Cd(p, n)^{111}In$  reaction [9] or the production of the PAC probe atom  $^{77}Br$ in Arsenic compounds via the  ${}^{75}As(\alpha, 2n){}^{77}Br$  reaction [10]. However, research in nuclear solid state physics demands a much larger variety of possible combinations of probe atoms and host lattices. Long-lived isotopes like <sup>111</sup>In or <sup>57</sup>Co produced, *e.g.*, at cyclotrons, and radiochemically separated from the target material can be either diffused or implanted into the crystal under study. Doping by diffusion is sometimes hampered by the surface barrier of the material or by small diffusion coefficients. In addition a deterioration of the crystal might be encountered, particularly in the case of compounds where the components strongly differ with respect to the partial vapour pressure (e.q., III-V semiconductors like GaAs or InP). However, in the cases where it works out, the diffusion technique provides advantages when compared to the implantation process such as a radiation damage free incorporation and low volume concentration, deeper doping profiles and greater homogeneity of the probe atoms in the sample. One of the successful examples is the doping of II-VI semiconductors (e.g. ZnO) with the PAC parent isotope  $^{111}$ In by diffusion [11, 12].

Doping by implantation is versatile since the radioactive isotopes can be implanted into any crystal. Off-line implanters dedicated to such an application are available, *e.g.*, at the universities of Göttingen and Bonn with maximum implantation energies of 400 keV and 160 keV, respectively. Many pioneering PAC experiments had only become possible due to the successful off-line implantation of <sup>111</sup>In into metals and semiconductors [13, 14]. Although implantation is the favorite doping technique, one has to keep in mind that radiation damage is its unavoidable compagnon. Therefore, suitable techniques for removing the radiation damage have to be explored for each combination of probe atom and host lattice prior to any other experiment. For obvious reasons both diffusion and off-line implantation are restricted to radioactive atoms with half-lives in the order of days.

Another type of implantation technique, the so-called recoil implantation was developped at the heavy ion accelerator VICKSI (ISL-Berlin) [15] and later on adapted to other machines like the TANDEM accelerator at the University of Erlangen [16]. A heavy ion, proton or He beam strikes a thin target and induces nuclear reactions. The reaction products are knocked out of the target with recoil energies up to several MeV and implanted into the host material (catcher foil). Due to the high recoil energy the implantation range is in the order of some  $\mu$ m. This doping technique also permits the use of short lived isotopes ( $^{111m}$ Cd,  $3/2^-$ state of  $^{57}$ Fe) and gives access to a rather wide range of different combinations of probe atoms and host lattices. However, the catcher samples may be contaminated by atoms from the target material or by products of competing nuclear reactions. Moreover, the production rates of the probe atoms are not very high as compared to an on-line implanter like ISOLDE at CERN in Geneva, and thus the beam times necessary for these types of experiments are rather long. Nevertheless many successful experiments are possible despite these drawbacks [16].

The most versatile tool for doping solid state samples with radioactive probe atoms is an on-line mass separator facility such as ISOLDE at CERN in Geneva. Whereas off-line separators only cover mass separation and implantation, the on-line mass separator comprises the production, the chemical separation, the mass separator and finally the implantation of radioactive isotopes into the sample within some few seconds [17]. At ISOLDE up to 600 different isotopes of 70 elements can be produced and the high intensity of up to  $10^{11}$  ions per second of those close to stability enable a wide range of solid state physics experiments. The implantation energy of 60 keV results in a projected range  $R_p$  for the isotopes of some tenths of nanometers below the surface.

#### 3. Experimental results and discussions

In the seventies most of the experiments applying nuclear techniques were focused on metals and defects in metals. This held in particular for PAC where the first studies of semiconductors only started in the beginnings of the eighties [18–20]. Already these first experiments revealed surprising results and theoretical models developed to interpret them are still valid [20]. However, many of the experiments and the interpretation of their outcome suffered from the sample preparation which at this time resulted mainly in polycristalline material. The breakthrough was reached by two parellel developments: (a) doping of well defined ZnO single crystals with <sup>111</sup>In probe atoms via diffusion [11,12] and (b) implanting <sup>111</sup>In ( $T_{1/2} = 2.81 d$ ) into Si single crystals [21].

#### 3.1. Donor-acceptor interaction

The II-VI compound ZnO is a wide-band gap semiconductor that crystallizes in wurtzite structure. The doping of the ZnO single crystals with the PAC probe atom <sup>111</sup>In is achieved by sprinkling commercially available, acid <sup>111</sup>InCl<sub>3</sub> solution onto the ZnO crystals. Afterwards, the sample is sealed into a quartz tube under atmospheric pressure and kept at 1300 K for about 15 hours. After this heating process the <sup>111</sup>In atoms are diffused into the crystal. The quadrupole hyperfine interaction is detected at the isomeric  $5/2^+$  state of <sup>111</sup>Cd which is populated by the Electron Capture decay of <sup>111</sup>In. PAC measurements revealed one electric field gradient (efg) in the case of pure ZnO crystals. It is characterized by a quadrupole coupling constant of  $\nu_Q = 31.2(1)$  MHz at room temperature and an asymmetry parameter of  $\eta = 0$ . The results are in agreement with calculations based on a modified point charge model which yield an axially symmetric field gradient ( $\eta = 0$ ) and a quadrupole coupling constant of 31.5 MHz for Cd atoms on substitutional Zn lattice sites in ZnO. Because the recoil energy involved in the decay of <sup>111</sup>In to <sup>111</sup>Cd is too low to activate a lattice site change, the mother isotopes <sup>111</sup>In are also localized on substitutional Zn lattice sites. Summarizing, these early experiments proved that it is possible to localize PAC probe atoms on well-defined lattice sites in semiconductors by the diffusion process [11, 12].

ZnO crystals that had been predoped with Na and Li during the crystal growth revealed two different electric field gradients: one experienced by Cd probe atoms localized on Zn-lattice sites within an ideal ZnO lattice structure ( $\nu_Q = 31.2$  MHz,  $\eta = 0$ ) and a second characterized by the PAC parameters  $\nu_Q = 115(1)$  MHz and  $\eta = 0.2(1)$ . This second eff is interpreted as follows: after the diffusion process <sup>111</sup>In is localized on substitutional Zn lattice sites. As group-III element replacing a group-II element (Zn), the probe atom In represents a donor due its excess of one valence electron as compared to the self atom Zn. The alkali metals Na and Li (group I) are also occupying Zn-lattice sites and act as acceptor impurities due to the lack of one valence electron as compared to Zn. During the diffusion process of the sample preparation both, the acceptors (Na, Li) and donors (In), are ionized due to the elevated temperature. The attractive Coulomb force leads to the formation of close acceptor-donor complexes by the trapping of mobile Na and Li acceptors at the In donors. By comparing the PAC data with theoretical calculations based on a modified point charge model. the microscopic structure of the In-acceptor and Cd-aceptor complex (see Fig. 1), respectively, could be deduced [11, 12].

These successful PAC experiments opened a new approach to donoracceptor interaction studies in semiconductors on a microscopic scale. Compared to Electron Paramagnetic Resonance Spectroscopy (EPR) or Infrared Spectoscopy (IR), the nuclear technique PAC is less variable with respect to the choice of probe atoms, but it is not limited to paramagnetic centers or in temperature. Moreover, PAC is very sensitive to the total number of complexes: already  $10^{11}$  to  $10^{12}$  complexes are a sufficient number to be detected. Consequently, similar PAC experiments in *n*-type Si followed very soon and the formation of different complexes between In acceptors and donors such as P, As, Sb and Bi could be investigated [21].



Fig. 1. Microscopic structure of complexes formed by Cd probe atoms and Na acceptors in ZnO. The Na acceptors are trapped by the positively charged donor <sup>111</sup>In, but the configuration is observed by PAC after the decay of <sup>111</sup>In to <sup>111</sup>Cd [11,12].

*N*-type Si doped with different group-V elements was implanted with <sup>111</sup>In. Afterwards an isochronal annealing programme was performed, resulting in the removal of the radiation damage and the formation of close complexes of In acceptors and group-V donors. In all cases well defined electric field gradients were observed at room temperature that could be unambigously assigned to In-P, In-As, In-Sb and In-Bi pairs. In addition, complexes were detected caused by the trapping of two donor atoms at the probe atom In (In-P<sub>2</sub> and In-As<sub>2</sub> complex) [21]. PAC experiments performed in n-type Ge yielded similar findings [22].

In a further set of experiments the probe atom <sup>111</sup>In was diffused into n-type Si. This process is rather complicated and involves the so-called silicon direct bonding process [23]: after hydrophilizing the surfaces of two Si wafers, <sup>111</sup>In was applied to one of them. The bonding was performed by keeping the samples for several hours at temperatures between 1200 K and 1500 K. Subsequent PAC measurements at room temperature proved the formation of In-donor complexes. PAC measurements revealed a strong temperature dependence of the efgs that characterize the close acceptor donor pairs formed by the probe atom (<sup>111</sup>In $\rightarrow$ <sup>111</sup>Cd) and a P, As, or Sb atom (see Fig. 2).

The drastic change in the strength of the efg cannot be explained by thermal lattice expansion or by phonons but by a model [20] which takes



Fig. 2. Temperature dependence of the electric quadrupole coupling constant  $\nu_Q$  for Cd-donor pairs in Si. The influence of the donor concentration in Sb-doped samples is visible above 600 K. The values measured at low temperatures are identical within the experimental accuracy (~ 1 MHz) [24].

into account that the ionization induced charge transitions at an electrically active center influences its efg. In case the active center represents a deep level, the charge carriers contributing to the conductivity are localized in the neighbourhood of the dopant atom. The electrically active center is produced by the radioactive decay of <sup>111</sup>In into <sup>111</sup>Cd, which transforms an inactive In-D pair (D: P, As, Sb) into a Cd-D (D: P, As, Sb) acceptor. The Fermi level is governed by the donors (P, As, Sb) that are present in higher concentration than the acceptors (<sup>111</sup>In, <sup>111</sup>Cd, <sup>111</sup>Cd-D). At low temperatures the acceptors are ionized and the efg corresponds to a Cd-D<sup>-</sup> charge state. With increasing temperature the ionization probability decreases and the charge state is characterized by a dynamic equilibrium between Cd-D<sup>-</sup> and Cd-D<sup>0</sup>, resulting in fluctuating field gradients. The temperature dependence of the efg is determined by the Fermi statistics and Fig. 2 shows the results of a fit of this theory to the data [24]. An advanced version of this dynamic model was developed later [25] and its application yields the energy levels  $E_A$  of the Cd-D acceptors which are about  $E_A = E_V + 0.5(1)$  eV.

## 3.2. Hydrogen passivation and diffusion in III-V semiconductors

Hydrogen is one of the most important impurities in semiconductors, both from the technical and the scientific point of view. It appears ionized  $(H^+, H^-)$ , atomic  $(H^0)$ , stable molecular  $(H_2)$ , metastable molecular  $(H_2^*)$  or precipitated (H-platelets) [26,27] and this rather puzzling behaviour poses problems in understanding processes like complex formation and hydrogen diffusion.

Hydrogen passivation in III-V semiconductors. The concept of hydrogen passivation of donors or acceptors comprises the formation of next nearest, electrically inactive hydrogen-dopant pairs. Due to the Coulomb interaction  $H^+$  ( $H^-$ ) ions are trapped at the ionized acceptors  $A^-$  (donors  $D^+$ ). The two different charge states compensate each other, the resulting complexes are electrically inactive and the resistivity of the semiconductor increases.

Since the late 80s many perturbed angular correlation experiments have been carried out on hydrogen in Si [28,29] and III-V semiconductors [6,30] and a considerable amount of new information could be provided concerning formation, microscopic structure and stability of acceptor hydrogen complexes. PAC studies on acceptor-hydrogen interaction require the doping of the material with probe atoms representing acceptor impurities in the corresponding semiconductor. For Si this demand can be easily fulfilled by using the common PAC probe atom <sup>111</sup>In $\rightarrow$ <sup>111</sup>Cd ( $T_{1/2} = 2.8$  d). Similar investigations in III-V semiconductors, however, poses a bigger problem, since <sup>111</sup>In as group III element does not represent an electrically active impurity. Fortunately, the PAC probe atom <sup>111m</sup>Cd $\rightarrow$ <sup>111</sup>Cd ( $T_{1/2} = 45$  min) exists, which represents an acceptor in III-V semiconductors and which is available at ISOLDE as isotopically clean ion beam with sufficient high intensity ( $\sim 10^9$  at/s).

After <sup>111m</sup>Cd implantation and annealing the III-V semiconductor samples were hydrogenated by two different charging techniques: plasma charging and low-energy H<sup>+</sup> implantation. Whereas the plasma-charging technique might suffer from the coproduction of lattice defects and problems concerning reproducibility, a low-energy and mass-separated proton beam avoids the formation of defects and an unwanted contamination of the samples.

The first hints of hydrogen-correlated complexes formed at the <sup>111m</sup>Cd acceptor were obtained after hydrogen-plasma charging of undoped GaAs and InP [30]. Very soon PAC experiments on plasma charged, undoped InAs and GaP as well as on InSb followed [31], and well-defined efgs have been observed in all materials. These findings were confirmed by PAC experiments in samples hydrogenated by low-energy proton implantation: GaAs, InP, InAs, GaP and very recently GaN were investigated after proton implantation at energies between 150 eV and 400 eV and doses between  $10^{14}$  and  $10^{16}$  cm<sup>-2</sup> [6,32]. In H<sup>+</sup>-implanted GaAs, InAs and GaP samples the same two configurations (f1(H), f2(H)) could be observed as in plasma-charged crystals, but in InP only f1(H) appeared. In GaN two different hydrogen-correlated complexes (f1(H),  $f1(H)^*$ ) have been found.

Control experiments in GaAs and InAs after Ar<sup>+</sup> (150 eV,  $10^{14}$  cm<sup>-2</sup>) and He<sup>+</sup> (1 keV,  $3 \cdot 10^{14}$  cm<sup>-2</sup>) implantations, respectively, did not reveal the formation of any complex at all. This very strongly supports an interpretation of f1(H) and f2(H) in terms of complexes formed by the trapping of the positively charged donor H<sup>+</sup> at the negatively charged acceptor Cd<sup>-</sup>. According to the experimental findings, the complex f1(H) is identified as Cd-H pair. Its axially symmetric efg tensor ( $\eta = 0$ ) indicates an axially symmetric complex and the Cd-H pair is the most simple configuration fulfilling this requirement. The  $\langle 111 \rangle$  orientation of the efg tensor corresponds to a  $\langle 111 \rangle$  lattice orientation of the Cd-H pairs. In GaAs, InAs, InP and GaP the crystallographic orientation and the stability of the Cd-H pairs support a model proposed by Pajot [33] which favours H on the bond-centre site, forming H-P and H-As bonds instead of an acceptor-hydrogen bond. In GaN complex f1(H) and  $f1(H)^*$  reflects the wurtzite structure of the material: both are Cd-H pairs, but oriented into different lattice directions [32].

**Hydrogen diffusion**. In the last few years, the breakthrough in the development of a specific laser ion source at ISOLDE enables PAC experiments on <sup>117</sup>Cd which open the access to the study of free hydrogen migration in III-V semiconductors.

InAs, InP and GaAs have been implanted with 60 keV <sup>117</sup>Ag atoms. After the decay of all <sup>117</sup>Ag atoms ( $T_{1/2} = 73$  s) into <sup>117</sup>Cd ( $T_{1/2} = 2.4$  h), the radiation damage was removed and <sup>117</sup>Cd-H pairs were formed by low energy H<sup>+</sup> ion implantation. The experimental conditions for annealing and hydrogenation were optimized according to the knowledge obtained by the investigations on <sup>111m</sup>Cd. The radioactive acceptor <sup>117</sup>Cd decays into <sup>117</sup>In, where the PAC measurement takes place. After the chemical transmutation from Cd into In, the PAC probe atom no longer represents an acceptor but either a constituent (InAs, InP) or an isovalent impurity (GaAs). In InAs and InP the H is no longer bound to the PAC probe atom by Coulomb force and diffuses freely. The single diffusion jumps out of the next neighbourhood of <sup>117</sup>In can be observed by PAC as a function of temperature. The first experiments revealed that H is still present in the immediate neighbourhood of the <sup>117</sup>In probe atom at 10 K and 78 K after the radioactive decay. At 78 K in GaAs and InAs the fraction of probe atoms with H in the neighbourhood decreases. This indicates that H already starts diffusing within the short time window of observation of about 100 ns, which is determined by the life time of the isomeric  $3/2^+$  state of <sup>117</sup>In. The mean time which H needs to perform a first diffusion jump is determined by the temperature and an analysis of the preliminary data for InP and GaAs yields an activation enthalpy for the H diffusion of about 200 meV [35]. This value is in agreement with data obtained for muon diffusion in GaAs [36], but significantly lower than those obtained by macroscopic techniques [37].

# 3.3. Optical studies of Au and Pt in Si

With the exception of some early, promising attempts [38] the trend to combine radioactive isotopes with common semiconductor-physics techniques only started at the beginning of the 90s. The very first experiment combining DLTS and radioactive isotopes was performed using the system Au and Pt in Si [39]. Later, optical methods like radioactive PL have been developed. Whereas the system Cd in GaAs was studied after off-line implantation of <sup>111</sup>In $\rightarrow$ <sup>111</sup>Cd in Konstanz [40], first PL experiments on Au and Pt in Si were launched at ISOLDE [41].

*N*-type Si ( $[P] = 10^{15}$  cm<sup>-3</sup>) was implanted with 60 keV <sup>191</sup>Hg and <sup>195</sup>Hg isotopes. After the decay into <sup>191</sup>Pt and <sup>195</sup>Au, respectively, the implantation damage was removed by annealing the samples for 5 s at 1173 K. The PL spectra, however, surprisingly revealed recombination lines which have been assigned to Ag (in case of <sup>191</sup>Pt) and Fe (in case of <sup>195</sup>Au) in earlier publications. But with increasing time, the intensity of the "Ag"-line decreased with a time constant corresponding to the half life of <sup>191</sup>Pt ( $T_{1/2} = 2.9$  d) whereas the same line appears during the radioactive decay of <sup>195</sup>Au into Pt (see Fig. 3). The intensity of the Fe related lines decreases with the radioactive decay constant of <sup>195</sup>Au into <sup>195</sup>Pt. Therefore the PL line which is commonly assigned to Fe is most probably caused by Au-Fe complexes, and the former "Ag" line is found to be Pt related. An unambiguous identification demands more experiments on radioactive Au and Pt in Si, but already after these few pilot PL experiments new results could be obtained on a system which has been studied for nearly 40 years.



Fig. 3. PL spectra of Si doped with  $^{191}$ Pt and  $^{195}$ Au. In both cases a clear time dependent change of the PL spectra can be observed. (a) shows the results of the chemical transformation of  $^{195}$ Au into  $^{195}$ Pt and (b) for  $^{191}$ Pt into  $^{191}$ Ir [41].

#### 3.4. Site-selective doping of semiconductors

Radioactive isotopes can be also used for a well-defined, site-selective doping of crystals. Here, the chemical transmutation involved in the  $\beta$  or electron-capture decay of the corresponding radioactive atoms forces the dopant on the desired lattice site. At ISOLDE this technique was applied to increase the doping efficiency in II-VI semiconductors. The impurity Ag is known to act as an acceptor in CdTe when occupying Cd lattice sites. But doping CdTe with Ag by conventional techniques like diffusion turns out to be not very efficient: although SSMS (Spark Source Mass Spectroscopy) detects between 10<sup>17</sup> and 10<sup>19</sup> Ag atoms cm<sup>-3</sup> only up to 1 % of these Ag atoms act as acceptors [42].

Therefore a new approach of doping was tested at ISOLDE: the transmutation doping of CdTe by implanting  $^{107}$ Cd, decaying into  $^{107}$ Ag within 6.5



Fig. 4. CV measurements of the time dependent increase of the acceptor density in p-type CdTe following the transmutation of <sup>107</sup>Cd into <sup>107</sup>Ag [42].

hours. The <sup>107</sup>Cd ions were implanted at 60 keV up to a dose of  $10^{12}$  cm<sup>-2</sup> into CdTe. Immediately after the implantation the radiation damage was removed by annealing the samples at 450°C and 600°C, thus ensuring that <sup>107</sup>Cd will be localized in the Cd sublattice after this treatment. Since the recoil energy involved in the  $\beta$ -decay is very small, the daughter dopant <sup>107</sup>Ag should occupy Cd sublattice sites after the radioactive decay, too. Fig. 4 shows the results of Capacitance–Voltage measurement. CV is not sensitve to the region close to the surface and therefore only a part of the Gaussian-shaped implantation profile can be observed. The measurements reveal that the implantation profile has broadened due to diffusion and that the number of acceptors is increasing with time, matching the half life of <sup>107</sup>Cd (6.5 h). Finally, nearly all <sup>107</sup>Cd atoms have transmuted into <sup>107</sup>Ag acceptors, indicating a doping efficiency of nearly 100 % [43].

## 4. Conclusion

Solid state physics with radioactive atoms can be performed in many different ways, ranging from the very cost-effective way of diffusing commercially available isotopes into the crystal under study up to the high-end technique of on-line implantations at ISOLDE. Besides the already appreciated nuclear techniques the number of conventional techniques using radioactive isotopes is increasing. Nowadays even proposals for EPR measurements on radioactive doped samples had been submitted to the ISOLDE Scientific Committee, underlining the prosperity of solid state physics with radioactive isotopes.

#### REFERENCES

- G. Schatz, A. Weidinger, A. Gardener, Nuclear Condensed Matter Physics: Nuclear Methods and Applications, 2nd edition, John Wiley and Sons, New York 1996.
- [2] D. Forkel-Wirth, Rep. Progr. Phys., to be published.
- [3] G. Langouche, J.C. Soares, J.P. Stoquert (ed.) Nuclear Methods in Semiconductor Physics, North Holland Elsevier Science Publishers B.V., Amsterdam 1992 and references therein.
- [4] G. Langouche (ed) Hyperfine Interaction of Defects in Semiconductors, Elsevier Science Publishers B.V., Amsterdam, 1992 and references therein.
- [5] M. Deicher, *Hyp. Int.* **79**, 681 (1993).
- [6] M. Deicher, W. Pfeiffer in: Hydrogen on Compound Semiconductor; Materials Science Forum, S.J. Pearton (ed), Vol. 148-149, Trans Tech Publications, Aedermannsdorf 1994, p. 481.
- [7] T. Wichert, Hyp. Int. 97-98, 135 (1996).
- [8] D. Forkel-Wirth, Phil. Trans. Roy. Soc. 356, 2137 (1998).
- R. Keitel, W. Engel, H. Föttinger, D. Forkel, M. Iwatschenko-Borho, F. Meyer, W. Witthuhn, Hyp. Int. 15/16, 425 (1983).
- [10] F. Lohmann, T. Schäfer, M. Wehner, R. Vianden, Mat. Sci. For. 143-147, 1155 (1995).
- [11] D. Forkel, H. Föttinger, M. Iwatschenko-Borho, F. Meyer, W. Witthuhn, H. Wolf, Mat. Res. Soc. Symp. Proc. 46, 304 (1985).
- [12] H. Wolf, S. Deubler, D. Forkel, H. Föttinger, M. Iwatschenko-Borho, F. Meyer, M. Renn, W. Witthuhn, R. Helbig, *Mat. Sci. For.* **10-12**, 557 (1986).
- [13] J. Christiansen (ed), Hyperfine Interactions of Radioactive Nuclei, Springer Verlag, 1983 and referencess therein.
- [14] Th. Wichert, M. Deicher, G. Grübel, R. Keller, H. Skudlik, Appl. Phys. A48, 59 (1989).
- [15] R. Sielemann, Y. Yoshida, *Hyp. Int.* 68, 11 (1991).

- [16] N. Achtziger, H. Gottschalk, T. Licht, J. Meier, M. Rüb, U. Reislöhner, W. Witthuhn, Appl. Phys. Lett. 66, 2370 (1995).
- [17] H. L. Ravn, Phys. Rep. 54, 201 (1979).
- [18] H. Barfuss, G. Boehnlein, H. Hohenstein, W. Kreische, H. Niedrig, A. Reimer, Z. Phys. B45, 193 (1982).
- [19] R. Kalish, M. Deicher, G. Schatz, J. Appl. Phys. 53, 4793 (1982).
- [20] D. Forkel, W. Engel, M. Iwatschenko-Borho, R. Keitel, W. Witthuhn, *Hyp. Int.* 15/16, 821 (1983).
- [21] Th. Wichert, M.L. Swanson, A.T. Quenneville, Phys. Rev. Lett. 57, 1757 (1986).
- [22] D. Forkel, N. Achtziger, A. Baurichter, M. Deicher, S. Deubler, M. Puschmann, H. Wolf, W. Witthuhn and ISOLDE collaboration, *Nucl. Instrum. Methods* B63, 217 (1992).
- [23] R. Lindner, R. Helbig, V. Lehmann, R. Hoffmann-Tikkaffin, P.A. Glasow, Europ. Mat. Res. Soc. 16, 373 (1987).
- [24] N. Achtziger, A. Baurichter, S. Deubler, D. Forkel, H. Plank, M. Puschmann, H. Wolf, W. Witthuhn, *Mat. Sci. Eng.* B4, 169 (1989).
- [25] N. Achtziger, W. Witthuhn, Phys. Rev. B47, 6990 (1993).
- [26] J.I. Pankove, N.M. Johnson, (eds.) Hydrogen in Semiconductors, Semiconductors and Semimetals vol. 34, Academic Press, San Diego 1991.
- [27] S. J. Pearton, (ed.) Hydrogen in Compound Semiconductors, Materials Science Forum Vol. 148-149, Trans Tech Publications, Aedermannsdorf, 1994.
- [28] Th. Wichert, H. Skudlik, M. Deicher, G. Gruebel, R. Keller, E. Recknagel, L. Song, Phys. Rev. Lett. 59, 2087 (1987).
- [29] A. Baurichter, S. Deubler, D. Forkel, W. Witthuhn, H. Wolf, Inst. Phys. Conf. Ser. 95, 471 (1989).
- [30] A. Baurichter, M. Deicher, S. Deubler, D. Forkel, H. Plank, H. Wolf, W. Witthuhn, Appl. Phys. Lett. 55, 2301 (1989).
- [31] A. Baurichter, M. Deicher, S. Deubler, D. Forkel, H. Plank, H. Wolf, W. Witthuhn, Appl. Surf. Sci. 50, 165 (1991).
- [32] A. Burchard, M. Deicher, D. Forkel-Wirth, E.E. Haller, R. Magerle, A. Prospero, R. Stötzler, in: III-V Nitrides, ed. F.A. Ponce, T.D. Moustakas, I. Akasaki, B.A. Monnemar, Mat. Res. Soc. Symp. Proc. Vol. 449, Pittsburgh 1997, p. 961.
- [33] B. Pajot, Inst. Conf. Ser. 95, 437 (1989).
- [34] D. Forkel-Wirth, N. Achtziger, A. Burchard, J.G. Correia, M. Deicher, T. Licht, R. Magerle, J.G. Marques, J. Meier, W. Pfeiffer, U. Reislöhner, M. Rüb, W. Witthuhn, Semi-insulating III-V Materials, ed. M. Godlewski, World Scientific, Singapore 1994, p. 267.
- [35] A. Burchard, M. Deicher, D. Forkel-Wirth, M. Knopf, R. Magerle, A. Stötzler, V.N. Fedoseyev, V.I. Mishin, in: *Hydrogen in Semiconductors and Metals* ed. N.H. Nickel, W.B. Jackson, R.C. Bowman, R.G. Leisure, *Mat. Res. Soc. Symp*, *Proc.* 513, 171 (1998).

- [36] R. Kadono, R.F. Kiefl, J.H. Brewer, G.M. Luke, T. Pfitz, T.M. Riseman, B.J. Sternlieb, *Hyp. Int.* 64, 635 (1990).
- [37] J. Chevallier in Ref. [27], p. 219.
- [38] I. Broser, K.-H. Franke, J. Phys. Chem. Sol. 26, 1013 (1965).
- [39] J. W.Petersen, J. Nielsen, Appl. Phys. Lett. 56, 1122 (1990).
- [40] R. Magerle, *Phys. Rev. Lett.* **75**, 1594 (1995).
- [41] M.O. Henry, S.E. Daly, C.A. Frehill, E. McGlynn, C. Msdonagh, E. Alves, J.C. Soares, D. Forkel in 23rd International Conference on the Physics of Semiconductors, ed. M. Scheffler, R. Zimmermann, Berlin 1996, Vol. 4. p. 2713.
- [42] J. Bollmann, M. Wienecke, J. Röhrich, H. Kerkow, J. Cryst. Growth 159, 384 (1996).
- [43] J. Bollmann, K. Maass, B. Reinhold, J. Röhrich, M. Wienecke, D. Forkel-Wirth, J. Cryst. Growth 161, 82 (1996).