Radioactive isotopes in solid state physics

Manfred Deicher
Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany
The ISOLDE Collaboration, CERN, CH-1211 Geneva 23, Switzerland

Nuclear physics has developed a number of experimental techniques for detecting particles or γ-radiation emitted during the decay of radioactive isotopes. The radioactive decay also opens the possibility to detect with high sensitivity the interaction of nuclear moments with external electromagnetic fields. Many of these techniques have successfully entered the field of condensed matter physics often labelled as "nuclear solid state physics" [1,2]. The first application of radioactive isotopes in solid-state physics research dates back to 1920, when radioactive Pb atoms were used by G. v. Hevesey to study self diffusion in lead [3]. Hevesey also first used radioactive atoms to study biologic systems by tracking the flow of radioactive tracers from plant roots to the leaves. The "radio tracer diffusion" technique was born. Nowadays it is a common method for investigating atomic diffusion processes in solids. An important advantage of employing radioactive nuclei is the ability of detecting signals from very small amounts of impurity atoms. This is particularly important for the characterization of semiconductors or surfaces where already a very low concentration of impurity atoms has a significant influence on the properties of the system. An especially useful tool represents the nuclear transmutation process caused by the β-decay of radioactive atoms since this process effects a change of the chemical properties of the respective atoms in a solid on a well-known time scale determined by the decay constant and therefore all properties (i.e. conductivity, luminescence) connected to the chemical nature of the impurity atoms should also change. The choice of a radioactive atom for a specific experiment is on the one hand determined by its chemical nature and on the other hand by its nuclear properties. The host system under study can be doped with these radioactive "probe" atoms either by diffusion, nuclear reaction or ion implantation. The probe atoms interact with their lattice surroundings and the information on these interactions is transmitted to the outside world by the emitted decay products and gives access to internal electric and magnetic fields in crystals, to lattice sites of the probe atoms, to diffusion processes, and to interactions between the probe atoms and other defects present in the crystal.

The ongoing experiments in solid state physics using radioactive ion deal with a wide variety of problems involving bulk properties, surfaces and interfaces in many different systems like semiconductors, superconductors, surfaces, interfaces, magnetic systems, metals, and ceramics. This article can highlight only a few examples to illustrate the potential of the use of radioactive isotopes for various problems in solid state physics. For more extensive reviews of the field see [2,4].

Getting the radioactive isotopes

The radioactive isotopes used can be produced at reactors or accelerators. For a few lucky cases of combinations of probe atoms and host lattices the samples can be doped directly via nuclear reactions inside the material. However, research in solid state physics demands a large variety of combinations of probe atoms and host lattices. Long-lived isotopes can be produced at cyclotrons and radio chemically separated from the target material. Then these isotopes can be either diffused or implanted into the material under study. The most versatile procedure is ion implantation: Depending on the implantation energy, the concentration of dopants, their lateral and their depth distribution can be controlled easily. Any unwanted co-doping by other elements is only determined by the purity of the ion beam and ion implantation is a process not limited by thermal equilibrium, therefore doping is possible beyond any solubilities. But, the energies used for implantation (keV to MeV) are much higher than typical binding energies of atoms in a crystal (eV) so that high concentrations of intrinsic defects (vacancies, interstitials, antisites, dislocations, even amorphous layers) are created. A thermal annealing treatment of the implanted crystal is required in order to remove these defects.

The most versatile "isotope factory" is represented by an on-line isotope separator facility such as ISOLDE at CERN in Geneva [5]. Here, the production, the chemical separation, the mass separation and the implantation of radioactive isotopes are integrated into one device (figure 1). At ISOLDE the radioactive isotopes are produced by spallation, fragmentation or fission reactions in solid or liquid targets hit by an external high energy proton beam. More than 600 different isotopes of 70 elements can be produced. The big success of the on-line mass separation technology at ISOLDE in many fields, nuclear and atomic physics, astrophysics and solid state physics, triggered worldwide interest in installing similar facilities for the production of radioactive ion beams [6].

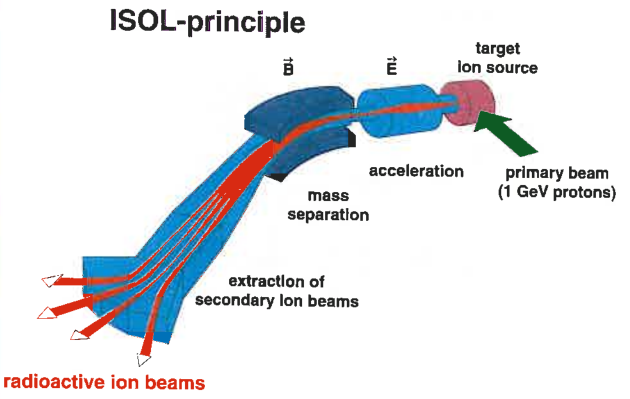

Fig. 1: The basic ISOL (Ion Separation On-Line) principle: Radioactive nuclides are produced by spallation, fission or fragmentation reactions triggered within a thick target by an external proton beam of 1 GeV. The target is kept at high temperatures permitting the rapid diffusion of the reaction products into the ion source where they get ionized by plasma, laser excitation or surface ionization. The singly charged ions are then accelerated, mass separated in a magnetic field and finally available for experiments at different beamlines.

Doping of semiconductors

Progress in semiconductor technology is driven by two requirements: Developing new materials with unique optical or electrical features and reducing the size of the individual constituents of an integrated device. These requirements demand a thorough understanding and control of defects responsible for the properties of these materials, both of intrinsic defects, such as vacancies, self-interstitials, or anti-sites, and of extrinsic defects, such as dopants and impurity atoms. As a consequence, a strong effort in basic and applied research is devoted to the investigation of defects and the electrical activation of dopant atoms for may different semiconductors: Elemental semiconductors (e.g. Si,, Ge, and diamond), III-V (GaAs, GaN), II-VI (ZnSe, CdTe), and IV-IV semiconductors (SiGe, SiC). Like stable isotopes, radioactive isotopes used as dopants influence the electronic and optical properties of semiconductors according to their chemical nature. Moreover, the properties of a semiconductor are not only determined by the chemical nature of a dopant but also by its location in the crystal lattice. Experimental and theoretical tools are needed for identifying the properties of defects, the diffusion mechanisms being responsible for the mobility of defects and the strengths of the mutual interactions between dopant atoms and intrinsic as well as extrinsic defects. Depending on the material and the smallest structural size used in a device, the electrical and optical properties can be already significantly altered by a defect which is present at a concentration as low as 10^{12} cm^{-3}. Therefore, the reliable control of the performance of semiconductors requires experimental techniques that combine high sensitivity to low defect concentrations with chemical sensitivity to the nature of the defects involved. Two of these techniques involving radioactive atoms will be presented here:

For decades, the most straightforward technique for locating impurity atoms within a lattice has been the so-called ion beam channeling effect, where an external ion beam (e.g. a He^+ beam with an energy of several MeV) is steered by small angle Rutherford scattering along atomic rows or planes of the crystal ('channels'). Using this technique, the detection of impurities is limited to concentrations of at least 10^{18} cm^{-3}. The sensitivity of techniques based on the channeling effect can be improved by several orders of magnitude by using radioactive impurity atoms located inside the crystal under study that emit charged particles (β^-, β^+, conversion electrons, α), the so called emission channeling technique [7]. Detecting the emission of these particles along different major lattice directions results in different emission yields compared to the observation along a random lattice direction (figure 2). For the case of electrons, an enhanced emission yield along a certain lattice direction is always the sign of an emitting atom residing on or near this lattice row which guides the electrons toward the surface. A reduced yield or the absence of an increased yield along a major axis hints at an interstitial site of the emitting atom. Observing the emission along different lattice direction allows the determination of the lattice site of the emitting atom with an accuracy of a few tenth of an Ångstrom.

Along with Fe, Ni, and Co, the element Cu is the most common but unwanted transition metal impurity in silicon devices. It interacts with various dopants and other defects, thereby changing the electrical effects of dopants. Positively charged Cu is the fastest known interstitial diffuser in Si. At high temperatures the solid solubility of Cu in Si is the highest among all transition metals but it is negligible at room temperature. As a consequence, Cu shows a strong tendency to react with various defects. Using the sensitivity of the emission channeling technique, the first direct determination of the lattice location of Cu in Si became possible (figure 3) [8]. The experiments showed, that after the implantation of ^{67}Cu into As-doped Si followed by an annealing at 600 °C, 90% of the Cu atoms are located close to substitutional lattice sites with a slight displacement of 0.5 Å

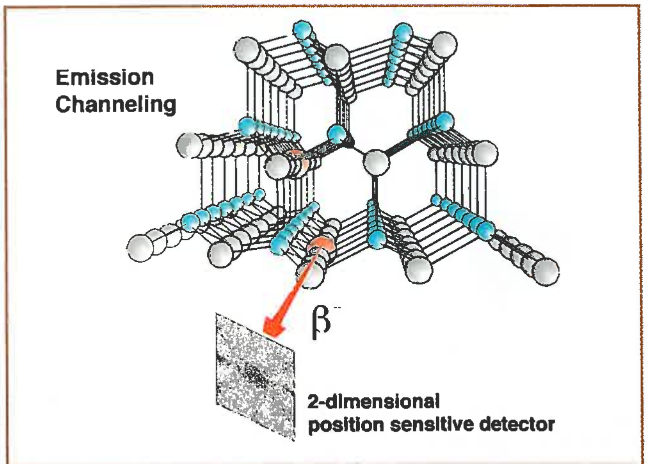

Fig. 2: Emission channeling of electrons (β^-) emitted from radioactive atoms on a lattice row: The electrons are steered along the lattice row leading to an enhanced emission yield (recorded by a 2-dimensional electron detector) along the lattice rows and planes compared to random lattice directions.

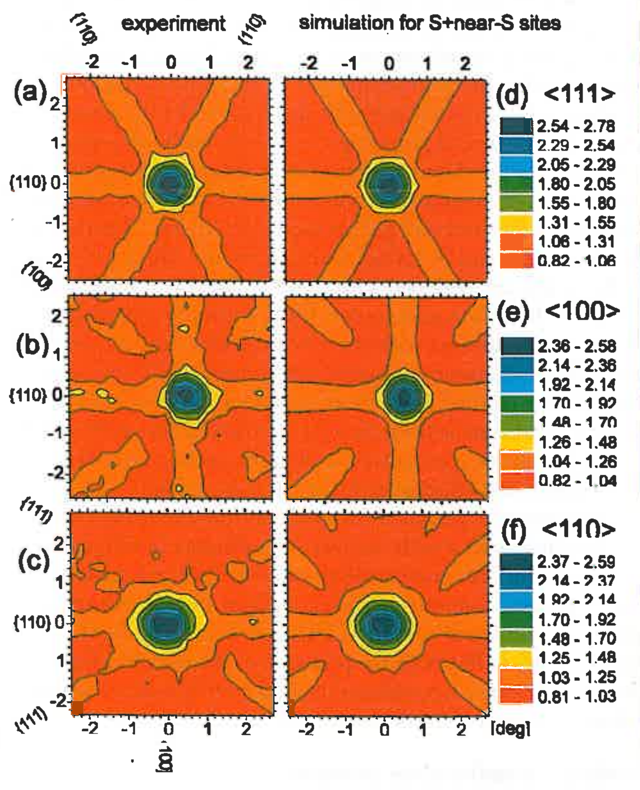

Fig. 3: Experimental emission yields of electrons emitted by ^{67}Cu in the vicinity of {111} (a), {100} (b), and {110} (c) directions in As doped Si after annealing at 600°C. Panels (d), (e), and (f) show simulated patterns of the experimental yields, corresponding to 90% of Cu close to substitutional lattice sites with a displacement of 0.5 Å [8].

From the application point of view, the electrical and optical properties of a semiconductor as determined by the presence of dopants and defects decide on the feasibility of a device. To determine these properties, a set of very accurate techniques like photoluminescence spectroscopy (figure 4) has been developed in semiconductor physics. All of them are perfectly feasible without any radioactive isotope, but they have often severe problems to identify the chemical nature of the defects which they are detecting. In combination with radioactive atoms, however, the element that gives rise to the observed electrical or optical properties can be unambiguously identified. If a change of an optical transition is due to a defect state in which the parent or daughter isotope is involved, the concentration of that defect will change according to the half-life of the radioactive decay. This time dependent change of the defect concentration has to show up in the corresponding intensity of the spectroscopic signal adding the lacking chemical information to the data delivered by photoluminescence spectroscopy.

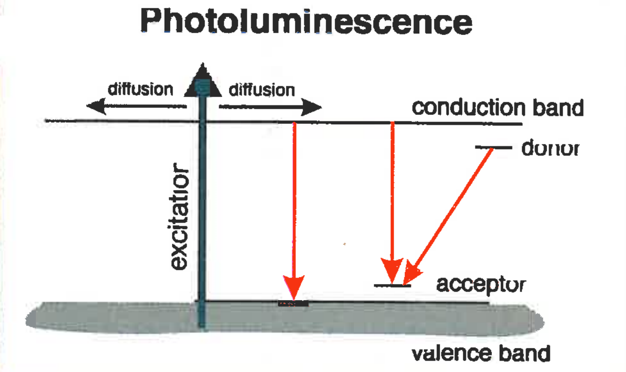

Fig. 4: Photoluminescence spectroscopy in semiconductors: At low temperatures, electrons are excited to the conduction band by a laser. The excited electrons diffuse through the lattice and finally recombine back to the valence band emitting light with an energy characteristic for the transition. The transitions can be a direct band-band transition, but can also involve donor or acceptor states present in the band-gap.

During the last years, there has been a great interest in the study of the wide band gap semiconductor GaN, mainly due to its potential applications in optoelectronics in the UV and blue spectral region. The aim of the following experiment, which will serve as an example for photoluminescence investigations with radioactive isotopes, was to uniquely identify the optical transitions created by Cd and Ag in GaN [9]. GaN was doped by ion implantation with radioactive ^{111}Ag at ISOLDE. In order to reduce the implantation induced damage, the sample was annealed at 1270 K. Figure 5 shows a series of photoluminescence spectra spectra recorded within 68 d after the doping. A strong photoluminescence band centered at 1.5 eV being not present before the doping became visible in the first spectrum recorded one day after implantation. Only weak luminescence could be observed between 2.4 eV and 3.3 eV. During the following 17 days, however, the intensity between 2.7 eV and 3.2 eV increased while the intensity of the 1.5 eV luminescence decreased. After 70 days, no luminescence at 1.5 eV could be detected any more and no further change of the spectrum has been observed. From this observations it is clear that the two energy regions, that exhibit a decreasing and increasing intensity as a function of time, have to be correlated with the elements Ag and Cd, respectively. Since no change should occur in the ^{111}Ag doped crystal besides the decrease of the Ag concentration and the increase of the Cd concentration, the vanishing luminescence at 1.5 eV has to be caused by recombination centers involving Ag. On the other hand, the two growing PL bands centered at 2.7 eV and 3.2 eV have to involve Cd defects.

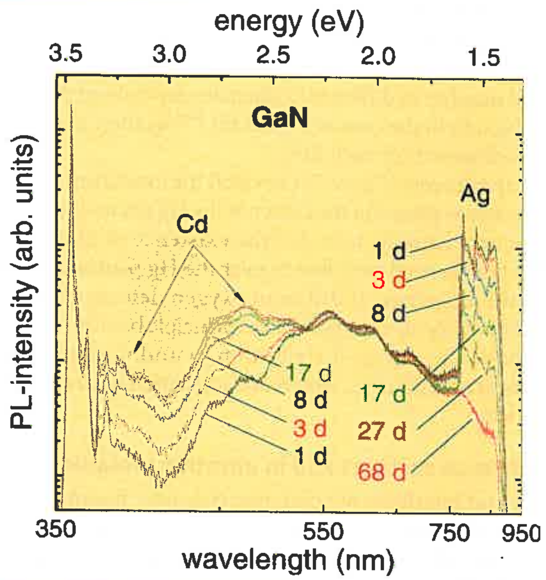

Fig. 5: Identification of optical states created by Ag and Cd in GaN: GaN has been doped with radioactive ^{111}Ag which decays to stable ^{111}Cd ($T_{1/2}$=7.45 d) and photoluminescence spectra have been recorded between 1 day and 68 days after the doping. The intensities of the photoluminescence transitions labeled Cd and Ag follow exactly the concentration changes due to the decay of ^{111}Ag and therefore these transitions must be caused by Ag and Cd, respectively [9].

High-T_c superconductors

Oxide materials have gained a great interest in fundamental and applied research due to their large variety of structural, electric and magnetic phenomena. Especially the discovery of the high-T_c superconductors triggered an intense experimental and theoretical research program for these systems. Among them, $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ represents the family of high temperature superconductors with the highest T_c. An exited nuclear state of the isotope ^{199}Hg can be used to characterize on an atomic scale the oxygen atoms (O_δ^{2-}), which are incorporated in the Hg-planes and dope the superconducting CuO_2 planes. So far, it has been shown that the doping concentration of O_δ^{2-} is about 1.5 higher than expected for the induced hole charge carriers. Furthermore, structural anomalies that are possibly related with the superconducting transition, have previously been observed (but not resolved) by neutron diffraction and EXAFS.

If the charge distributions around a nucleus in a lattice (^{199}Hg in this case) has a symmetry lower than cubic, an electric field gradient (EFG) is created at the site of the nucleus. This situation exists in non-cubic crystal lattices or in the presence of defects in the neighbourhood of the probe atom. The EFG, defined as the second spatial derivative of the electric potential and, therefore, being a tensor, contains information on the symmetry and the orientation of the charge distribution in respect to the crystal axis, and delivers information on the configuration of the defect causing the EFG. It interacts via the hyperfine interaction with the nuclear quadrupole moment of the probe nucleus and leads to a quadrupole splitting of the *m*-substates of the involved nuclear levels. A technique being especially suited for detecting EFG is the perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC) [1]. In a PAC experiment (figure 6), the precession frequency of the nuclear spin I is measured, which depends on the magnitude of the EFG. In addition to the EFG, the spin I and the nuclear quadrupole moment Q of the intermediate nuclear state of the isotope define the values of the observed frequencies. The observed number of different frequencies depends on the number of *m*-sublevels, in the case of $I = 5/2$ for ^{199}Hg, there are three frequencies observed for each EFG.

The experiments (figure 7) provided the local identification of single O_δ atoms placed in the center of the Hg planes [10]. In addition, the experiments revealed the existence of other, not yet identified oxygen-related defects near the Hg planes. The results proved the existence of different oxygen defects near the Hg planes. This work also triggered first-principle band structure calculations of the charge distribution in undoped and oxygen doped lattice structures, which are consistent with the experimental data.

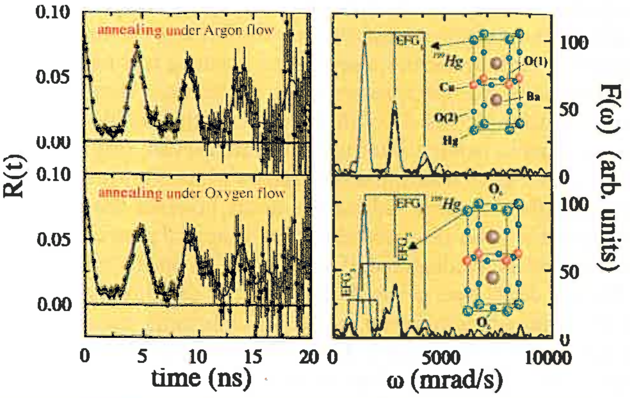

Fig. 7: Local environment of Hg atom in the high-T_c superconductor $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ observed by PAC spectroscopy using the isotope ^{199}Hg: PAC time spectra R(t) (left) have been measured under Argon flow (undoped material) and under oxygen flow (oxygen doped material). The pictures on the right show the corresponding Fourier transforms of the R(t) functions. In the R(t) and the Fourier spectra the blue lines represent the fit function and the Fourier transform of the fit function, respectively. The electric field gradient EFG2 could be assigned to oxygen sitting in the centre of the Hg channel, EFG3 is due to a still unknown oxygen related defect [10].

Magnetism at surfaces and in ultrathin metallic layers

Surfaces and interfaces of solid materials have become a field of tremendously growing interest in several areas of physics, in particular in ultrathin metallic layer magnetism. The information on the variation of magnetic properties from atomic layer to atomic layer of ultra-thin multilayer systems or even from atom to atom in such a monolayer is of fundamental interest. Therefore, local structural and electronic properties of surfaces and at interfaces measured on the atomic scale are in the centre of many investigations [11].

One beam-line connected to the ISOLDE separator is designed for ultra-high vacuum, a prerequisite for surface and thin layer experiments. PAC spectroscopy can also detect magnetic hyperfine interactions with the high sensitivity which is required for studies of surfaces, ultrathin layers and interfaces [12]. Three pioneering experiments performed at ISOLDE have concentrated on Ni/Pd thin-layer systems, where induced magnetic interactions in Pd were investigated. The possibility to use different radioactive probe atoms on the same systems, for example *sp*-elements as ad-atoms on a nickel surface, allows the experimental test of detailed theoretical predictions. Recently, within epitaxially grown Pd layers on Ni surfaces, Pd or Cd PAC probe atoms were positioned in a controlled way at different distances from the interface. The different probe atom locations in such experiments are illustrated in figure 8. The measured static magnetic hyperfine interactions at Pd revealed a ferromagnetic ordering of

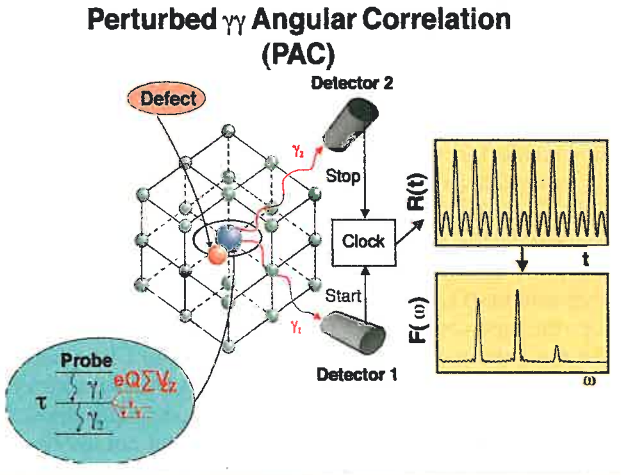

Fig. 6: A local electric field gradient V_{zz} created by a defect present in the neighbourhood of a radioactive probe atom interacts with the nuclear quadrupole moment of the probe nucleus. This interaction causes a precession of its nuclear spin which can be detected by recording the γ-quanta γ_1 and γ_2 in coincidence (perturbed angular $\gamma\gamma$ correlation, PAC). This results in a time spectrum R(t) which can be analyzed by calculating its Fourier transform F(ω). The observed frequencies are characteristic for a specific defect configuration.

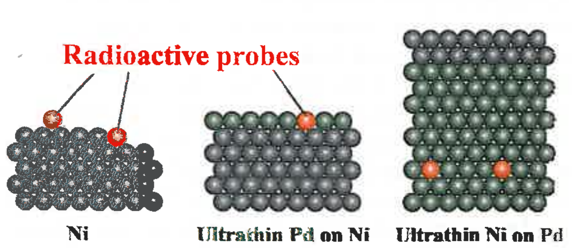

Fig. 8: Outline of three pioneering experiments using radioactive atoms performed at metallic surfaces and interfaces. Left: Radioactive probe atoms were positioned at different surface structures of Ni (e.g., terraces, steps) and, using PAC, the magnetic hyperfine fields were measured with an unsurpassed structural resolution. Centre: The 'ferromagnetic' behaviour of ultrathin Pd grown on Ni was investigated with different radioactive probe atoms. Right: Magnetic properties in Pd, induced by a coverage of an ultrathin Ni layer on Pd, were measured for different distances from the Ni/Pd interface.

the Pd layers of rather complex nature. By contrast, discrete hyperfine fields were measured for Cd probe atoms which could be attributed to specific lattice locations [13].

Conclusion

Radioactive isotopes are used in many different fields of solid state physics: semiconductors, surfaces and interfaces, magnetism, high-T_c superconductors, metals, ceramics. They provide as nuclear probes unique information about their local surroundings on an atomic scale. Due to the high sensitivity of the used spectroscopic techniques, they constitute an important tool for the determination of chemical nature, lattice location, thermodynamical properties, dynamical, electronic and optical behaviour of intrinsic and extrinsic defects in solids.

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