PROPOSAL TO THE ISOLDE AND NEUTRON TIME-OF-FLIGHT EXPERIMENTS
COMMITTEE (INTC)

Emission Mössbauer spectroscopy of advanced materials for opto- and nano- electronics

Aarhus – Milano – Reykjavik – Cape Town – Durban – Berlin – CERN – Leuven – RIKEN – Shizuoka – Sacavém – Porto – Lisbon

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Summary

Mössbauer Spectroscopy (MS) is a versatile solid state method giving information about probe atom interactions with its nearest neighbours. Simultaneously, information on the probe valence state, site symmetry, and electric and magnetic hyperfine interactions is obtained. MS can be applied in many different contexts in material science and solid state physics. MS using radioactive isotopes, applied for decades at the ISOLDE facilities, has the particular merit of very high sensitivity. This opens up many new possibilities compared to traditional (absorption) Mössbauer spectroscopy. Among them is the possibility of working with very low concentrations ($< 10^{-4}$ at. %), where the probe atoms are true dilute impurities. Here we propose four main themes in our Mössbauer investigations for the coming years: (1) Paramagnetic relaxations in compound semiconductors; (2) Vacancy diffusion in group IV semiconductors; (3) Doping of Si-nano-particles; (4) Investigation of phase change mechanisms in chalcogenides.

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Introduction

In home laboratories Mössbauer spectroscopy is usually applied on samples containing stable Mössbauer isotopes (e.g. ^{57}Fe or ^{119}Sn) with "long" lived radioactive sources (^{57}Co ($T_{1/2} = 270$ d) and ^{119m}Sn ($T_{1/2} = 290$ d)) that are commercially available. Useful samples for such experiments, however, require a concentration of the probe atoms ≥ 0.1 at. %. Under such conditions the probe atoms may interact, and, where the solubility is low, unintentional precipitation can be a problem significantly limiting the physical applications.

Using samples with radioactive Mössbauer isotopes and resonance detectors enables working with much lower concentrations ($< 10^{-4}$ at. %). Furthermore working with short lived isotopes with lifetimes of minutes in on-line experiments (e.g. ^{57}Mn ($T_{1/2} = 1.5$ min) and ^{119}In ($T_{1/2} = 2.1$ min)) allows for studying interactions with defects generated in the implantation process in a concentration, time, and temperature region inaccessible by other methods.

Mössbauer spectroscopy differs from many other physics experiments performed at ISOLDE. In our case the property of the radioactive probe atoms is not of primary interest, it is applied as a tool to understand the material into which the probe atoms are implanted. As the number of materials is essentially infinite there are probably infinite applications of the method.

At present there are many different applications of interest to our collaboration. However, in this proposal our focus is on advanced materials that have potential opto-electronic applications. The proposed experiments fall under four main themes whose scientific significance, for clarity, are presented and discussed separately below.

The group utilizing ^{57}Mn isotopes (internally called the ^{57}Mn Mössbauer Collaboration at ISOLDE/CERN) consists of specialists from 11 institutes around the world. The experimental equipment is stored at ISOLDE and the set-up is installed for each beam time. We apply a multi-purpose implantation chamber where we can perform measurements at different sample orientations, in different external magnetic fields, and at high and low temperatures. Recent additions to our setup include better external magnetic field measurements and new data taking equipment. A picture of the set-up and implantation chamber is shown in Fig. 1.
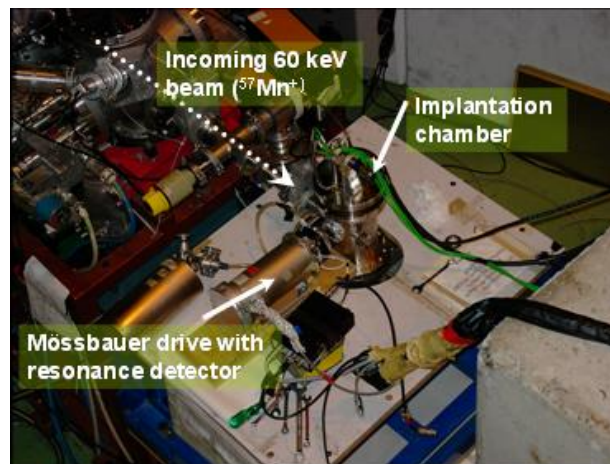
Fig. 1: Picture of the implantation chamber used for Mössbauer measurements of short lived isotopes in configuration used for elevated temperatures. Sample holder is attached to the lid and different lids are used for the different applications.

Currently the group has beam-time through the IS443 experiment entitled "Mössbauer studies of dilute magnetic semiconductors". We have decided not to apply for an addendum to this proposal as we have basically disproved the presence of dilute (ferro)magnetism in the systems that were studied. Some additional measurements are needed to verify some of the new findings that will make use of the three ^{57}Mn shifts left. The expected use of the remaining shifts is listed in Table 1:

Table 1: Estimated use of the remaining shifts from the IS443 proposal. Based on the experimental plan for 2009 that was never fully implemented.

Measurement	Time needed (h)
GaN at low temperatures	3
Pre-implanted ZnO after annealing, dose dependence and temperature series	4
Pre-implanted ZnO after annealing, angular measurements at RT	3
CdO measurements at elevated temperatures	1.5
CdO measurements at low temperatures	3
NiO measurements at low temperatures	3
Ga doped ZnO, dose dependence and high temperatures	3
LaAlO$_3$ at high temperatures	1.5
Calibration	2
Total	**24 hours**

In the past several years we have focused on the use of the ^{57}Mn$^+$ ($T_{1/2}$ = 1.5 m) beam that decays to the 14.4 keV Mössbauer state of ^{57}Fe. Experience tells us that we are able to make use of 4-6 shifts per year to conduct our physics exploration. In this new proposal we have expanded on the possible isotopes for Mössbauer spectroscopy to deal with new physics and making use of the growing Mössbauer collaboration.

New physics applications require use of the 23.8 keV Mössbauer state of ^{119}Sn. This state can be reached by many different isotopes produced at ISOLDE. Here we propose using ^{119m}Sn ($T_{1/2}$ = 290 d) for preparing samples that are used in measurements at home laboratories, ^{119}In ($T_{1/2}$ = 2.1 min) for on-line experiments, and ^{119}Sb ($T_{1/2}$ = 38 h) for off-line experiments to be performed at ISOLDE. Additionally to this ^{57}Co ($T_{1/2}$ = 270 d) may become a useful beam at ISOLDE, enhancing considerably the work that can be done with ^{57}Mn.

The expansion of the ^{57}Mn Mössbauer collaboration at ISOLDE/CERN in recent years makes it possible to utilize new beams by distribution of the work load. A description of the group and specialties within the group are listed in Appendix 3.

Research themes:

1. Paramagnetic relaxations in compound semiconductors

Introduction

Dilute magnetic semiconductors, obtained by partial replacement of the cat-ions in conventional semiconductors by transition-metal ions, are of current interest as potential semiconductor-compatible magnetic components for spintronic applications. For ZnO, room temperature dilute magnetism has been predicted by theory [Dietl00] and observed experimentally (see e.g. [Jung02]). However, the origin of magnetism of transition-metal doped ZnO is poorly understood [Koji06, Osgur05] and there are inconsistent reports in the literature. Recently the role of defects have been discussed by many authors [Kapilashrami09, Khalid09, Wang08, Wang09], while others have suggested that the observed effects may be due to unintentional precipitation [Potzger09, Zhou09].

Using ^{57}Mn to populate the Mössbauer state in ^{57}Fe and local concentration $< 10^{-4}$ at. % concerns about precipitation are obviated. Further by performing measurements in an external magnetic field we have developed methods for distinguishing between ferromagnetism and slow relaxation paramagnetism. An example of such a result is shown in Fig. 2.
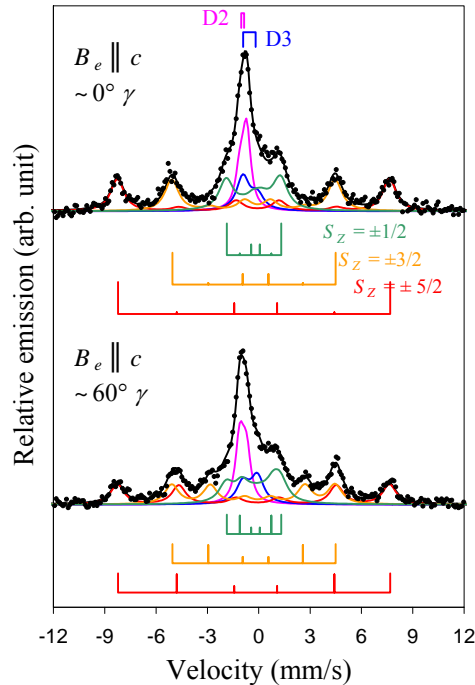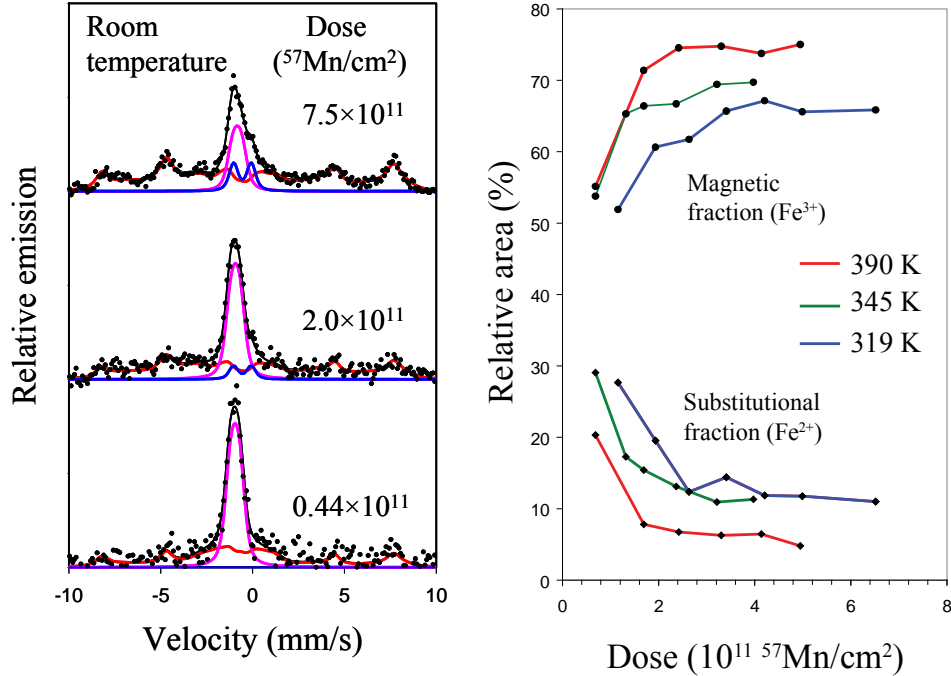

Fig. 2: Room temperature Mössbauer spectra of ^{57}Fe obtained after implantation of ^{57}Mn in ZnO. The spectra are obtained in ~0.7 T external magnetic field oriented with respect to the γ-quanta as indicated (from [Gunnlaugsson10]).

In the spectrum measured at 60º, small features are seen at $v \sim -3$ mm/s and $v \sim 2.5$ mm/s that clearly disappear in the spectrum measured at 0º. This is characteristic for the disappearance of the lines belonging to the $\Delta m_I = 0$ transition for a $S_Z = \pm 3/2$ electronic state. Such a state can only exist in paramagnets (ferromagnets have only a spectrum resembling the spectrum

from the $S_Z = \pm 5/2$ electronic state). This result shows that the electronic spin of the Fe^{3+} atom is not coupled to lattice defects from the implantation nor to the lattice, which would result in fast spin-spin or spin-lattice relaxations. The absence of such couplings shows that the Fe^{3+} atoms is unlikely to act as the seed needed for the proposed (long range) ferromagnetism.

Although we have measured many types of samples as part of the IS443 experiment ZnO is the only type of material where dose dependence has been observed, i.e. where relative site fractions change upon implantation of ^{57}Mn (cf. Fig. 3).

Fig. 3: Left: Mössbauer spectra obtained at room temperature after implantation of the indicated dose of ^{57}Mn into ZnO. Area fractions of substitutional Fe^{2+} and Fe^{3+} at the temperatures indicated (from [Molholt09]).

Such dose dependence can be caused by implantation induced changes in the Fermi level making Fe^{3+} the more stable species, or due to capture of highly mobile charge compensating defects (V_{Zn} or O_I). Since Fermi level changes would be expected to depend only on the total dose, diffusion of vacancies as a thermally activated process should show strong temperature dependence as is observed (cf. Fig. 3).

The current experimental data suggest that defect capture is the most likely scenario. This has an interesting scientific implication, as it suggests that spin-spin relaxations with intrinsic defects are a slow process. However, this point can be better established by measurements in highly n-doped ZnO and different types of dose dependence experiments. These measurements are among those to be conducted within the remaining shifts of the IS443 experiment.

Methods

By making use of the ^{57}Mn beam at ISOLDE/CERN we have now a straight-forward technique to distinguish between slow paramagnetic relaxations and ferromagnetism. We

want to apply this method in different types of material where dilute magnetism has been proposed and in relevant model systems. This list includes (but not restricted to) Al_2O_3, TiO_2, ZrO_2, HfO_2, ZnO, SiO_2, poly-crystalline ALD-ZnO, GaN, $SrTiO_3$, and MgO. In some cases (ZnO at least) additional measurements are needed to document dose dependence. Based on our experience with the ^{57}Mn beam each angular measurement takes ~½ hour, and for an experiment in which measurements are taken at 8 different angles would take ~4 hours. Tracking of dose dependence in a sample takes ~ ½ hour, so the estimated time required for 10 samples, taking into account a short break for the sample change, translates to approximately 6.5 ^{57}Mn shifts.

The dose dependence as has been observed for ^{57}Mn in ZnO can be monitored using implantation of ^{119}In ($T_{1/2}$ = 2.1 min) and emission Mössbauer spectroscopy measurements on the ^{119}Sn daughter nucleus. Indium is a shallow donor in ZnO and is likely in the In^{3+} state. N-In co-doped ZnO [Ye09] has been found useful to make a *p*-type material. Indium behaves probably differently from ^{57}Mn with respect of the capture of mobile structural defects. No ^{119}Sn Mössbauer spectroscopy has been performed in ZnO, so detailed mapping to determine sites and their properties will be necessary. Based on yield estimates, a good series of temperature dependent measurements on a single material takes one shift. Dose dependence at a single temperature takes of the order of an hour, and performing dose dependence at several temperatures and documenting the dose-rate dependence needs at least one shift. The measurements should be repeated in a relevant model system (e.g. MgO and/or Al_2O_3), so at least four shifts are needed.

To help in interpretation the spectra obtained by implantation of ^{119}In, at least two samples implanted with ^{119m}Sn should be prepared, for study in home laboratories where especially annealing studies and irradiation experiments can be performed. Additionally $e^- - \gamma$ PAC measurements on such samples can be performed at ISOLDE. Based on yield estimates one shift is required for the sample implantations.

Slow paramagnetic relaxations in oxide systems were studied intensively by Mössbauer spectroscopy in the late 1960's using dilute systems with stable ^{57}Fe to avoid spin-spin relaxations (see e.g. [Wickman66, Wickman66b, Wertheim64] and e. g. [Schunemann99] for a recent overview). The conclusions that can be derived from such studies were, however, hampered by the dilution required. Using radioactive probes, dilution is automatically achieved and spectra of much higher quality obtained. Among open questions is the absence of spin-spin relaxations where the probe atom is close to a structural defect, as we have observed in the systems studied under the IS443 proposal. This suggests that transition metal ions do not exchange spin with the defects and should therefore be considered isolated.

To examine the physics of the relaxation processes one would like/need to measure under different conditions than is possible in our on-line implantation chamber, and perform various irradiation/annealing studies as well. It is possible that this is best done with long-lived ^{57}Co ($T_{1/2}$ = 270 d). A source of this type should be prepared by implantation into ZnO, and at least one other model system, requiring two shifts assuming that one shift is needed to prepare a suitable sample.

## 2. Vacancy diffusion in group IV semiconductors

Introduction

Silicon is presently the most important material in semiconductor technology and is probably the most studied material in the world. Among the important impurities are transition metal ions that are difficult to avoid completely during crystal growth. Transition metal impurities have generally low solubility, and are fast diffusers in silicon, and have received major attention in the literature (see e.g. review [Istratov99] with 369 references). In previous experiments at ISOLDE, using ^{57}Mn, we have concentrated on the physics of the iron impurities in Si and other group IV semiconductors (see publications in appendix 1). In the present proposed project we wish to advance our investigations by using the implanted probe, to study some of the intrinsic properties of the silicon substrate.

There are still open issues on the fundamental properties of this material. Among them is the diffusivity of the mono-vacancy. The behaviour of the mono-vacancy is a determining factor for the diffusivity of many species in the material, and understanding its behaviour can lead to better methods to model the material at processing temperatures.

This work is partly motivated by the paper of Bracht *et al*. [Bracht03], who reported, that the diffusivity of the mono-vacancy in Si at elevated temperatures occurs with much higher activation energy (1.7(5) eV), than observed at low temperatures (0.25-0.45 eV [Watkins91]). It was suggested that this behaviour is related to the extensive nature of the vacancy at elevated temperatures, as originally proposed by Seeger and Chick [Seeger68], although their results are disputed [Suezawa08, Watkins08].

The findings of Bracht *et al*. [Bracht03] have been supported by Mössbauer investigations at ISOLDE, using implantation of ^{57}Mn, [Gunnlaugsson03, Weyer07]. We have applied ^{57}Mn ($T_{1/2}$ = 1.5 min) that decays to the 14.4 keV Mössbauer state of ^{57m}Fe ($T_{1/2}$ = 100 ns), giving the daughter Fe atom a recoil of average energy of 40 eV. At $T > 400 - 500$ K the implantation damage anneals during the lifetime of the ^{57}Mn (i.e. spectral fractions belonging to Fe in disordered surroundings are not present in the spectra) and the probe atoms are most likely present on substitutional sites and/or near-substitutional sites (U. Wahl, private communication, 2009). In the recoil the majority of the probe atoms are expelled to interstitial sites while simultaneously creating a vacancy. In previous publications we have monitored the diffusion of differently charged interstitial Fe [Gunnlaugsson02]. At elevated temperatures ($T > 600$ K) the vacancy and the interstitial Fe atom recombine, forming a meta-stable Fe_I-V pair [Gunnlaugsson03]. The rate of this recombination suggests a slow vacancy in accordance with the results of Bracht *et al*. [Bracht03]. In $Si_{1-x}Ge_x$ a transition from a slow vacancy to a fast vacancy is observed between $0.1 < x < 0.25$ [Gunnlaugsson10].

The broadening of a Mössbauer line, due to diffusion, is proportional to the diffusion jump rate, which is proportional to the macroscopic diffusion constant. Broadening due to pairing is proportional to the in-growth of the pair. Fig. 4 shows results obtained in Si and SiGe.
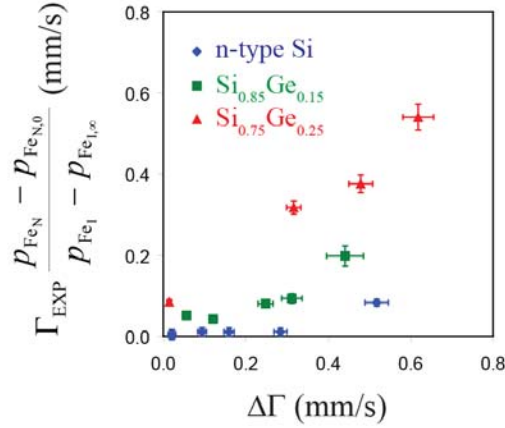
**Fig. 4: Scaled in-growth of Fe$_I$-V line vs. the line broadening of the interstitial spectral line.**

On the *x*-axis is plotted the observed broadening. On the *y*-axis is plotted the expected broadening due to pair formation. In pure Si none of the broadening can be explained by pair formation, suggesting that the interstitial Fe atom diffuses faster than the vacancy. In Si$_{0.75}$Ge$_{0.25}$ most – if not all – of the broadening is due to pair formation, suggesting that the vacancy diffuses faster than the interstitial Fe atom.

These findings show the strength of the method to distinguish the different mechanisms and to arrive at sound interpretations. If there were a general, slow recombination with mobile vacancies, the transition from slow to fast vacancies as a function of Ge content should not be observed. These findings are in accordance with the view, that at elevated temperatures the vacancy is a point defect in pure Ge and an extensive defect in pure Si [Seeger68].

Methods

The 1.5 min decay of ^{57}Mn offers an alternative way to study the diffusion of the vacancies in Si. This can be done by monitoring site fractions as a function of time using so-called time-delayed Mössbauer measurements [Gunnlaugsson09]. In these measurements we make use of short (1.5 min) implantation, and then record the spectra as a function of time in three to five time segments up to 8.5 minutes after the implantation. In test experiments we have observed a lowering of the substitutional fraction and an increase of the Fe-vacancy complexes (cf. Fig. 5).
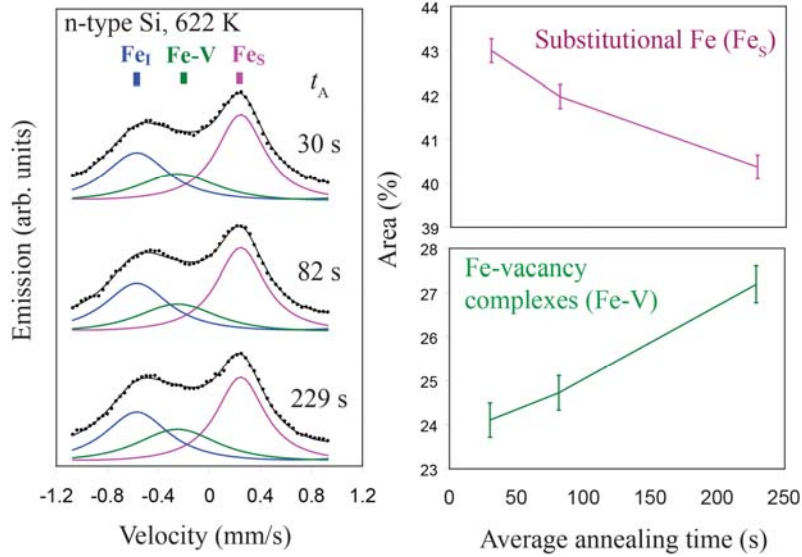
Fig. 5: Left: Time-delayed Mössbauer spectra obtained in n-type Si at 622 K. Average annealing times are indicated. Right: Site fractions obtained from simultaneous analysis of the spectra on the left. Interstitial fraction is not shown, but has roughly a constant area.

At low temperatures the mobility of the vacancies is insufficient to reach the Mn atoms prior to decay. A lowering of the substitutional fraction was not observed at room temperature [Weyer03]. At 622 K the mobility of the vacancies is at least high enough to ensure that some of the substitutional Fe recombines, forming an Fe-vacancy complex.

Mapping this behaviour as a function of temperature in different types of materials will give substantially new information on vacancy kinetics in Si based materials. For ^{57}Mn the time dependence should be fully mapped for at least 7 types of materials; intrinsic Si, n$^+$-type Si, p^{++}-type Si, Ge, and at least two $Si_{1-x}Ge_x$ compositions leaving one additional type/composition depending on the results obtained. For each type of material the general temperature dependence should be mapped. This is usually sufficient at temperatures above room temperature, with additional measurements where broadening of the interstitial line is observed. At least 3 hours should be budgeted for such characterizations. At strategic temperatures (at least 5) the time dependence should be obtained. From experience, we know that obtaining sufficient statistics requires repeating the measurements ~6 times, depending on the temperature and material, so each measurement takes an hour. At the lower temperatures some annealing has to be applied, to ensure that we re-start with a fresh sample and the correctness of the procedures for annealing have to be documented in at least one composition (4 h). This experiment gives a total sum of 60 hours needed or 7.5 shifts.

Complementary results can be obtained by utilizing implantation of ^{119}In ($T_{1/2}$ = 2.1 min) and Mössbauer spectroscopy on the 23.8 keV radiation from the ^{119}Sn daughter nuclei. Previous work using this isotope (and other isotopes decaying to the Mössbauer state of ^{119}Sn) have identified the Mössbauer spectra of sites related to implantation damage, substitutional Sn, interstitial Sn, and Sn-V complexes in Si and Ge [Weyer80a, Weyer80b, Weyer80c]. Indium behaves differently with respect of capture of vacancies and has a lower recoil energy than ^{57}Mn, resulting in a lower interstitial fraction. Therefore, the vacancies available originate not from the recoil production of interstitials and vacancies and interpretation of the results is slightly easier. We propose doing the same experiments as in Si with at least four samples, requiring 4 shifts.

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To help interpret the spectra obtained in the on-line experiments (^{119}In and ^{57}Mn) spectra, samples with ^{119m}Sn ($T_{\frac{1}{2}} = 290$ d) and ^{57}Co ($T_{\frac{1}{2}} = 270$ d) are highly helpful. This will enable us to perform irradiation studies and annealing studies to verify or test some of the findings from the on-line experiments. It is estimated that one sample per shift can be produced using ^{57}Co, and two good samples with ^{119m}Sn can be produced per shift, requiring two shifts for ^{57}Co implantation and one shift for ^{119m}Sn implantation.

Emission channelling

The findings from this part of the proposal will be greatly enhanced with emission channelling studies using ^{56}Mn ($T_{\frac{1}{2}} = 2.6$ h). The two techniques can compliment each other significantly and this has not yet been explored in detail. With emission channelling it is possible to monitor site fractions after short implantation. Emission channelling is sensitive to lattice locations in a different way than Mössbauer spectroscopy. While it is possible that we can not by means of Mössbauer spectroscopy distinguish between different types of Fe-vacancy defects, this may be readily possible with emission channelling. Arguments for the necessary complimentary experiments and beam time request is given by addendum to the IS453 experiment by U. Wahl.

3. Doping of Si-nano-particles

Introduction

Semiconductor nano-crystals are basis for new generations of devices [Lu07] with applications in e.g. solar-cells, printable electronics, and efficient light emitters. Excellent results with homogeneous nano-crystals of Si have been obtained by high temperature annealing (>1000ºC) of layers of Si in SiO$_2$. (cf. Fig. 6).
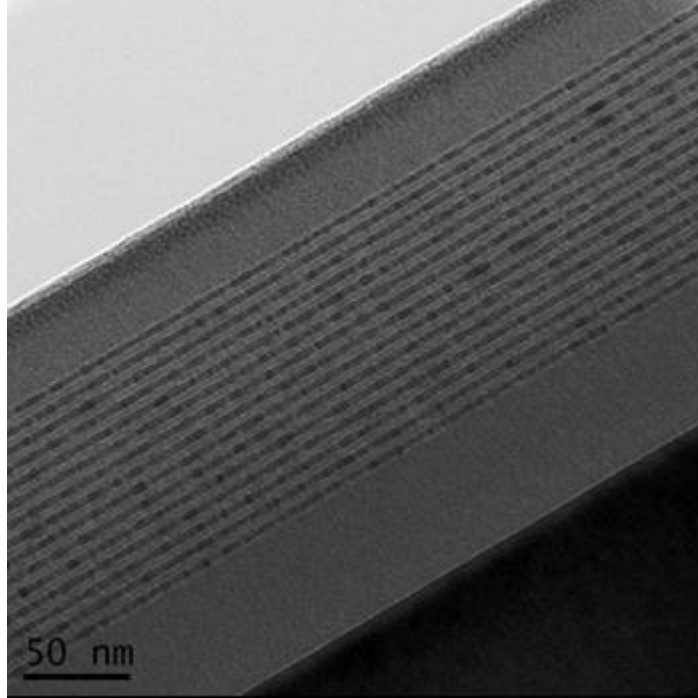
Fig. 6: TEM picture of annealed sample with Si layers, showing the formation of nano-particles within the matrix.

Among the current problems is obtaining n-type doping of the nano-particles in a consistent way (see e.g. [Norris08] and references therein). One potential route is by ion implantation (see e.g. [Murakami09]). This assumes that the dopant implanted into the matrix is not destroying the properties of the device and/or can be passivated, and that the dopant can be embedded into substitutional sites in the Si nano-particles. Antimony (Sb) is a possible n-type dopant. Its properties in the samples can be monitored with [119]Sn Mössbauer spectroscopy following implantation of [119]Sb ($T_{\frac{1}{2}} = 38$ h). The Mössbauer experiments can give insight into several parameters affecting the quality of the doping and the Si nano-particles. The Mössbauer spectrum of [119]Sn impurities in Si is well known from earlier experiments performed at ISOLDE [Weyer80a, Weyer80b, Weyer80c, Weyer82], giving us the possibility of determining the fractions belonging to substitutional Sn, Sn-V complexes, and Sn in amorphous surroundings due to the implantation damage. The Debye-Waller factor for each site can be determined giving information on the changes in bond lengths, and the position of spectral components can give information about the electronic structure.

The lifetime of the [119]Sb is favourable in this context as it allows for several experiments on each sample, such as annealing experiments to study the incorporation of the Sb dopants into the Si nano-particles, and measurements at different temperatures to determine site fractions and Debye-Waller factors.

Methods

Samples are made at the University of Århus (group of A. N. Larsen) with at least 30% volume of Si nano-particles and nano-particles with different average sizes. For random implantation (depending on the particle size) up to 20% of the probe atoms can be in interface sites of the matrix/nano-particles, leaving at least 25% in regular sites for detailed study. For obtaining useful data five samples have to be studied, virgin Si, virgin SiO_2, and at least three

types of Si nano-particles within SiO_2. The activity of each sample should be at a level of ~mCi, so according to the beam estimates two samples can be produced per shift, giving in total 2.5 shifts needed.

4. Investigation of phase change mechanisms in chalcogenides

Introduction

Chalcogenides are binary or ternary alloys formed with one or more elements belonging to group VI (e.g. Ge-Sb-Te, Ge-Te, Sn-Sb-Te), some of them showing rapid and reversible phase changes between amorphous and crystalline phases (above room temperature) under the influence of electric current pulses or laser stimulation. The structural changes in chalcogenides are accompanied by marked variation of electrical conductivity of several orders of magnitude and/or refractive index, making them of huge interest for application into data storage and non-volatile memory devices. In particular there is a relatively recent and renovated interest in chalcogenides for applications into novel devices in the next generation of non-volatile solid state memories (phase-change memories, PCM) [Lankhorst05], and for designing high capacity and ultra-performing optical memories like DVDs [Pieterson05]. The data read-out in PCMs is performed by reading the different electrical resistivity in the crystalline/amorphous phases, while in optical memories the reading is accomplished by monitoring the change in the film reflectivity in the different states. The most studied chalcogenide material is the stoichiometric $Ge_2Sb_2Te_5$ compound, for which the switching mechanism is particularly favourable and together with the doped Ge-Sb-Te and Ge-Te compounds, their application in the semiconductor industries is very promising [Lankhorst05, Pieterson05, Pirovano04, Wang04].

The phase changes in chalcogenides are due to structural transformations at the atomic scale, and the small volume of "active media" acts as a programmable resistor between the high and low resistance/reflectivity states. There are critical aspects related to the phase transition mechanism that remain unclear. The atomic scale origin and mechanisms across the structural transition have a tremendous interest from both the fundamental and technologically-relevant point of view. For example one of the major limits of PCM devices is the relatively high programming current, but a lower current could be used if a complete understanding of the mechanisms behind the transitions would be achieved. The effect of the doping of chalcogenides is another important issue, since the presence of dopants like In, Ge, Ga, and Sn, has been shown to influence the transition properties and the writing/erasing speed of chalcogenides [Pieterson05, Song07, Wang04], where the doping effects depends on the local structural changes in the alloys.

In the case of $Ge_2Sb_2Te_5$ it has been shown by extended x-ray absorption fine structure (EXAFS) that the crystalline↔amorphous transition is accompanied by a change of the local environment of Ge atoms from an octahedral to a tetrahedral local arrangement [Kolobov04]. Following the paper by Kolobov *et al.* [Kolobov04] a theoretical model was proposed where the mechanism of the transition was simulated for the $Ge_1Sb_2Te_4$ compound, confirming that the Sb local environment is basically not affected during transitions and that the principal mechanism governing the transition is the shift of Ge atoms back and forth along the Ge-Te direction [Welnic05].

The use of different stoichiometry, i.e. Sb-rich Ge-Sb-Te, when compared to the most explored $Ge_2Sb_2Te_5$, can lead to improved performances of chalcogenide-based devices [Yoon07]. Among other changes Yoon *et al.* [Yoon07] observed a slower crystallization rate in Ge-Sb-Te alloys upon increasing the Sb content. To our knowledge there are no reports concerning the underlying microscopic mechanism driving phase transitions in Sb-rich Ge-Sb-Te compounds, which could be not necessarily the same as demonstrated in $Ge_2Sb_2Te_5$ stoichiometric films [Kolobov04, Welnic05].

More recently a theoretical paper [Caravati07] demonstrated that, *"amorphous GST obtained by quenching from the liquid phase displays two types of short range order. One third of Ge atoms are in a tetrahedral environment while the remaining Ge, Sb, and Te atoms display a defective octahedral environment, reminiscent of cubic crystalline GST"*. The picture proposed by Caravati *et al.* [Caravati07] is slightly different than the model proposed in [Welnic05]; underlining that the atomic scale mechanisms driving the structural transitions in chalcogenides is still an open question. In particular, experimental techniques which are applicable to follow the transitions at the most atomic-scale would be highly fundamental for a full understanding of the phase transitions in chalcogenides of different compositions.

Methods

The use of ^{119m}Sn and ^{119}Sb radioactive beams at ISOLDE will enable us to perform ^{119}Sn Mössbauer spectroscopy at the Sn and Sb sites of implanted Ge-Sb-Te materials of different compositions. The annealing behaviour of the Sn/Sb implantation-induced damage in chalcogenides has to be investigated. The proposed experiments could be enormously important in order to elucidate the microscopic mechanisms driving the macroscopic phase transitions in chalcogenides by monitoring the atomic-scale changes around the Sn and Sb atoms via the hyperfine interactions of their nuclei with the surrounding neighbourhood. The relatively low total implanted dose excludes the possibility of clustering of the implanted species and the implanted Sn and Sb ions will therefore act as "external" probes of the thermally activated structural changes across the phase transitions in chalcogenides.

Chalcogenides thin films will be deposited at MDM National Laboratory by metal organic chemical vapour deposition (MOCVD). Different Ge-Sb-Te stoichiometry will be provided in order to investigate and understand the eventual differences in the atomic-scale structural transitions across crucial temperatures and in a wide temperature range, and for different material compositions.

We plan to compare the transition properties of $Ge_2Sb_2Te_5$, $Ge_{2-x}Sb_{2+x}Te_5$ (at least 4 samples of different compositions), and pure GeTe. This will be done by recording ^{119}Sn Mössbauer spectra at the Sn and Sb sites. As we estimate that two samples can be produced in each shift with these isotopes, 2.5 shifts for ^{119}Sb and 2.5 shifts for ^{119m}Sn isotope are needed.

Complementary measurements

Perturbed Angular Correlation

It is possible to perform e^-_γ Perturbed Angular Correlations (PAC) experiments on ^{119m}Sn [Soares73]. It is an excellent PAC 3/2 isotope where K or L conversion electrons from the first transition are used for triggering the start while the M1 γ used on Mössbauer experiments triggers the stop. A Siegbahn-type spectrometer, providing measurements from 30 K up to

800 K, is in operation at ISOLDE and is the ideal setup for performing such measurements. Samples would be prepared for both PAC and Mössbauer spectroscopy, allowing for direct comparison between the results obtained by both techniques. Measurement times are similar as with Mössbauer spectroscopy (~weeks). In case that the Mössbauer results are complicated, PAC may give information on their interpretation by determining values of the quadrupole interaction. Decisions on which samples would be potentially used for PAC will be taken on bases of the Mössbauer results.

Emission channelling

As mentioned under research theme 2, there are planned complementary Mn emission channelling experiments. See addendum to the IS453 experiment from U. Wahl regarding this part of the experiments.

Research project

We first list the shifts needed for each research theme. For practical purposes we suggest that this proposal will take over the remaining three IS443 shifts. Below, the information on the beams, and how the numbers in Tables 2 and 3 are derived are discussed.

Table 2: Beam request summarized for each research theme (number of shifts).

Theme	Isotopes					Total
	^{57}Mn	^{57}Co	^{119}In	^{119}Sn	^{119}Sb	
1. Paramagnetic relaxations in compound semiconductors	6.5	2	4	1		13.5
2. Vacancy diffusion in Si based semiconductors	7.5	2	4	1		14.5
3. Doping of Si nano-particles					2.5	2.5
4. Investigation of phase change mechanisms in chalcogenides				2.5	2.5	5
Calibration (~10%)	1.5		1			2.5
Contingency/opportunistic science (~20%)	2.5	1	2	0.5	1	7
Total	18	5	11	5	6	45

The total number of shifts would be taken in lumps of 7-11 shifts per year over the next 4-5 years depending on beam availability. Here we request roughly half of the shifts, and plan for an addendum in 2-3 years. In that time we expect to be able to give a status report of partial results, better information on beam quality to revisit the numbers in Table 2 and give the INTC the possibility of evaluating the progress. It is very likely that based on partial results, we will be interested in modifying the research project to optimize our use of the beam facilities. We plan on having concluded the research themes in this proposal before the shutdown due to the HIE-ISOLDE upgrade.

We may not necessarily need all types of isotopes every year. The number of research themes and their overlap gives us good flexibility. In some cases we want to obtain partial results one year in order to be able to optimize the experiments for the next year/opportunity.

It should be emphasized that the quality of the data will only be as good as the calibration of the setup. For the on-line measurements we would like to budget the necessary calibration

within the proposal. The aim of the calibration is the following: (1) Measure standards to obtain channel/velocity relationship, (2) Determine detectors effectiveness (amount of Be in windows, noise reduction of detectors), and (3) Make sure all parameters are optimized in the data collection. For the off-line studies these parameters are determined independently without the use of implanted sources. To fully make sure on the quality of the setup a few hours per beam time are needed, estimated to be around 10% of the beam time needed.

We would also like to budget contingency/opportunistic science. All proposed experiments that we have performed at ISOLDE have been initiated by allowing short time for opportunistic science. This has ensured that when we propose experiments we know that the systems that we are interested in studying can give the results we are seeking for. Researchers around the world, within the Mössbauer community, are aware of the possibilities at ISOLDE, and we are often approached with performing short implantations to answer specific questions. Though the results are not always positive, this has often resulted in publications and new collaborations. Under this term, we would also place the contingency, in case the beam quality is reduced and more time is needed to obtain the data than we have accounted for. If new scientific results are obtained during the beam time, this will give us the possibility of exploring these in details. It should be emphasized that the many of the projects proposed here were unknown only few years ago, and without a doubt, new physics can be explored that we are unaware of at this time. We suggest that an addition of ~20% beam time request to the proposed experiments will give us fully the opportunities needed.

Beam request

The table below summarized the use of ~½ of the shifts needed to conclude the research program outlined above. A total of 22 shifts are requested here, and it is suggested that (if successful) the new experiment will take over the remaining IS443 shifts. The shifts will be used in lumps of 7-11 shifts per year over the next 2-3 years.

Table 3: Formal beam request.

Isotope	Minimum Intensity/µC	Energy	Shifts	Target	Ion source
^{57}Mn (1.5 m)	$(2\text{-}3)\times10^{8}$	≥ 50 keV	9	UC$_\text{x}$	Mn RILIS
^{57}Co (270 d)^{a}	9×10^{7}	≥ 50 keV	3	ZrO$_2$ or YtO$_2$	VADIS
^{119}In	$(2\text{-}3)\times10^{8}$	≥ 50 keV	5	UC$_\text{x}$	In RILIS, or W surf. Ionized
^{119m}Sn	1×10^{9}	≥ 50 keV	2	UC$_\text{x}$	Sn RILIS
^{119}Sb^{b}	4×10^{8}	≥ 50 keV	3	UC$_\text{x}$	Sb RILIS
Total			22		

^{a}We take all nuclei that eventually decay to ^{57}Co ($^{57}_{\geq27}$X).

^{b}Impurities should be below ~10%, Tellurium impurities (^{119}Te ($T_{1/2} = 4.7$ d) have to be avoided.

Beam details

^{57}Mn ($T_{\frac{1}{2}}$ = 1.5 min.)

This is the beam the group is very familiar working with. The measurements are done online in the setup described in the introduction of the present proposal. Our experience for the last several years is that we use roughly 5-6 shifts per year of ^{57}Mn.

^{57}Co ($T_{\frac{1}{2}}$ = 270 d)

^{57}Co has been of interest for implantation by the Mössbauer collaboration for long time. Unfortunately it has not become available elsewhere, and production at ISOLDE may be the first opportunity for us with a ZrO_2 or YtO_2 target and VADIS ion source. Yields are unknown, but we can make use of all isotopes that eventually decay to ^{57}Co. For beam requirements, we assume having a sample with minimum activity (~3 μCi) within one shift to make this useful. Assuming 1.6 μC/s of protons this translates to ~$9\times10^7/\mu$C. If such a beam is not available, it is still possible to make use of weaker sources (down to 0.5 μCi) by working with more compact Mössbauer set-up and allowing geometrical broadenings, work only at low temperatures and accept lower statistics.

^{119}Sb ($T_{\frac{1}{2}}$ = 38 h)

Due to the lifetime the samples should be implanted, and taken for measurements and annealing at ISOLDE. Recent technical additions, at the solid state laboratory at ISOLDE, make this a favorable way of doing the measurements. Chambers for making measurements at low temperatures exist in Aarhus and will be transported to ISOLDE, and either the on-line chamber or a new chamber will be used for measurements at temperatures above room temperature.

^{119}Sb can be produced with an UC_x target and a Sb RILIS ion source. ^{119}In impurities decay quickly and will not disturb the measurements. About $4\times10^8/\mu$C for ^{119}Sb are estimated [Koster09].

Another possibility is using a LaC_x target and a MK5 ion source, but this will produce more ^{119}Te, which has a half live of 4.7 days and would therefore hamper studying the Sb behavior in the systems we are interested in [Koster09].

^{119m}Sn ($T_{\frac{1}{2}}$ = 290 d)

Implantations would be performed at ISOLDE and measurements and annealing in home laboratories.

^{119m}Sn can be produced with an UC_x target and a Sn RILIS ion source. Yields of ^{119}Sn have been measured $1.8\times10^9/\mu$C [Koster08]. Both the ^{119g}Sn and ^{119m}Sn are produced, but $1.0\times10^9/\mu$C of ^{119m}Sn can be expected with some background of ^{119}Cs and ^{119}In, but not at a disturbing level [Koster09].

Molecular beams are not suitable for our measurements.

Production with LaC_x target and Sn RILIS ion source is a possibility with yield of ~ $1.3\times10^7/\mu$C of ^{119m}Sn [Koster09]. This, however, requires much longer implantation time, but would be an option to prepare a weak source if the implantation can be done parallel with other experiments and the UC_x target and Sn RILIS is not available [Koster09].

^{119}In ($T_{1/2}$ = 2.1 min)

^{119}In has a very similar half live as ^{57}Mn, and the same setup can be used.

^{119}In can be produced with an UC_x target and an In RILIS ion source. Yields have not been estimated, but should be similar to those of ^{119m}Sn ($>1\times10^9/\mu C$) [Koster09]. Some contamination of ^{119g}In should be present, but does not matter in our case (decays to ^{119m}Sn).

Another method is with an UC_x target and a W surface ionizer. This would give a loss of a factor of 3 compared to the In RILIS ion source (i.e. $3\times10^8/\mu C$), but can be favored as it is very easy to get such a beam scheduled, since most targets used for UC_x + RILIS will do the job. So while the lasers are prepared for another run one can use the targets with the surface ionized In beams [Koster09] working with intensity we are used to from our ^{57}Mn experiments.

Sample preparation

For the long lived isotopes (^{57}Co and ^{119m}Sn) experience (G. Weyer, private communication) is that a source strength of ~3 µCi is the minimum required for having a useful source to use in the laboratory (10-20 measurements of sufficient quality during 1 year). This means that total number of implanted atoms should be 3.75×10^{12} for ^{57}Co. Budgeting one shift to make such a sample, and assuming 1.6 µC/s proton beam result in a requirement of $> 9\times10^7$ /µC.

In the case of ^{119m}Sn the beam quality at ISOLDE allows us to request a good source strength (~15 μCi), with a total dose just below where the transition threshold from amorphous pockets to amorphous layers (around 5×10^{13} cm^{-2}, see e.g. [Weyer82]). With the beam estimates it will be possible to produce two such samples per shift.

For ^{119}Sb, we estimate that for a single implantation, we should have a starting activity of about 10 mCi, which is enough to perform ~10 good measurements within ~70 hours. This requires ~7.3×10^{12} atoms implanted, and is well below the amorphization limit. With the above estimate of ~$4\times10^8/\mu C$ ^{119}Sb/s, the making a suitable sample takes of the order of 3-4 hours allowing the preparation of two samples per shift.

References

[Bracht03] H. Bracht, J. Fage Pedersen, N. Zangenberg, A. Nylandsted Larsen, E. E. Haller, G. Lulli and M. Posselt, <u>Radiation Enhanced Silicon Self-Diffusion and the Silicon Vacancy at High Temperatures</u>, *Phys. Rev. Lett.* **91** (2003) 245502, doi: 10.1103/PhysRevLett.91.245502.

[Caravati07] S. Caravati, M. Bernasconi, T. D. Kühne, M. Krack and M. Parrinello, <u>Coexistence of tetrahedral- and octahedral-like sites in amorphous phase change materials</u>, *Appl. Phys. Lett.* **91** (2007) 171906, doi: 10.1063/1.2801626.

[Dietl00] T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, <u>Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors</u>, *Science* **287** (2000) 1019-1022, doi: 10.1126/science.287.5455.1019

[Gunnlaugsson02] H. P. Gunnlaugsson, G. Weyer, M. Dietrich, the ISOLDE collaboration, M. Fanciulli, K. Bharuth-Ram and R. Sielemann, <u>Charge state dependence of the diffusivity of interstitial Fe in silicon detected by Mössbauer spectroscopy</u>, *Appl. Phys. Lett.* **80** (2002) 2657-2659, 10.1063/1.1469216.

[Gunnlaugsson03] H. P. Gunnlaugsson, G. Weyer, N.E. Christensen, M. Dietrich, M. Fanciulli, K. Bharuth-Ram, R. Sielemann, A. Svane, and the ISOLDE

Collaboration, <u>On the kinetics of the formation of interstitial Fe-vacancy pairs at high temperatures</u>, (2003) *Physica B,* **340-342** (2003) 532-536, doi: 10.1016/j.physb.2003.09.141.

[Gunnlaugsson09]   H. P. Gunnlaugsson, G. Weyer, R. Mantovan, D. Naidoo, R. Sielemann, K. Bharuth-Ram, M. Fanciulli, K. Johnston, S. Olafsson, G. Langouche, <u>Isothermal defect annealing in semiconductors investigated by time-delayed Mössbauer spectroscopy: Application to ZnO</u>, *Hyp. Int.* **188** (2009) 85–89, doi: 10.1007/s10751-008-9893-4 .

[Gunnlaugsson10]   H. P. Gunnlaugsson *et al.*, Paramagnetic Fe defects in ZnO (working title), *Appl. Phys. Lett.* (2010) In prep.

[Istratov99] A. A. Istratov, H. Hieslmair, E. R.Weber, <u>Iron and its complexes in silicon</u>, *Appl. Phys. A* **69** (1999) 13–44, doi: 10.1007/s003399900059

[Jung02]   S. W. Jung, S.-J. An, Gyu-Chul Yi, C. U. Jung, Sung-Ik Lee, and S. Cho, <u>Ferromagnetic properties of $Zn_{1-x}Mn_xO$ epitaxial thin films</u>, *Appl. Phys. Lett.* **80** (2002) 4561, doi:10.1063/1.1487927.

[Kapilashrami09]   M. Kapilashrami, J. Xu, V. Ström, K. V. Rao, and L. Belova1, *Appl. Phys. Lett.* **95**, 033104 (2009), doi: 10.1063/1.3180708.

[Khalid09] M. Khalid, M. Ziese, A. Setzer, P. Esquinazi, M. Lorenz, H. Hochmuth, M. Grundmann, D. Spemann, T. Butz, G. Brauer, W. Anwand, G. Fischer, W. A. Adeagbo, W. Hergert, and A. Ernst, *Phys. Rev. B* **80**, 035331 (2009), doi: 10.1103/PhysRevB.80.035331.

[Koji06]   A. Koji, <u>Seeking Room-Temperature Ferromagnetic Semiconductors</u>, *Science* **312** (2006) 1883, DOI: 10.1126/science.1125461.

[Kolobov04]A. V. Kolobov, P. Fons, A. I. Frenkel, A. L. Ankudinov, J. Tominaga and T. Uraga, <u>Understanding the phase-change mechanism of rewritable optical media</u>, *Nature Mat.* **3** (2004) 703/708, doi:10.1038/nmat1215

[Koster08] U. Köster, O. Arndt, E. Bouquerel, V. N. Fedoseyev, H. Frånberg, A. Joinet, C. Jost, I. S. K. Kerkines, R. Kirchner, the TARGISOL Collaboration, <u>Progress in ISOL target–ion source systems</u> , *Nucl. Instr. Meth. B* **266** (2008) 4229–4239, doi:10.1016/j.nimb.2008.05.152.

[Koster09] Ulli Köster, Private communication, 2009

[Lankhorst05] M. H. R. Lankhorst, Bas W. S. M. M. Ketelaars and R. A. M. Wolters, <u>Low-cost and nanoscale non-volatile memory concept for future silicon chips</u>, *Nat. Mater.* **4** (2005) , 347-352, doi:10.1038/nmat1350.

[Lu07]   W. Lu and C. M. Lieber, Nanoelectronics from the bottom up, *Nature Mater.* **6** (2007) 841-850.

[Murakami09] K. Murakami, R. Shirakawa, M. Tsujimura, N. Uchida, N. Fukata, S. Hishita, <u>Phosphorus ion implantation in silicon nanocrystals embedded in SiO_2</u>, *J. Appl. Phys.* **105** (2009) 054307.

[Norris08] D. J. Norris, A. L. Efros, S. C. Erwin, <u>Doped Nanocrystals</u>, *Science* **319** (2008) 1776, doi: 10.1126/science.1143802

[Mølholt09] T. E. Mølholt, R. Mantovan, H. P. Gunnlaugsson, K. Bharuth-Ram, M. Fanciulli, H. P. Gíslason, K. Johnston, Y. Kobayashi, G. Langouche, H. Masenda, D. Naidoo, S. Ólafsson, R. Sielemann and G. Weyer, <u>Temperature and dose dependence of defect complex formation with ion-implanted Mn/Fe in ZnO</u>, *Physica B* **404** (2009) 4820-4822, doi: 10.1016/j.physb.2009.08.187.

[Osgur05]   Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho and H. Morkoç, <u>A comprehensive review of ZnO materials and devices</u>, *J. Appl. Phys.* **98** (2005) 041301, DOI: 10.1063/1.1992666.

[Pieterson05] L. van Pieterson, M. H. R. Lankhorst, M. van Schijndel, A. E. T. Kuiper and J. H. J. Roosen, <u>Phase-change recording materials with a growth-dominated crystallization mechanism: A materials overview</u>, *J. Appl. Phys.* **97** (2005) 83520, doi:10.1063/1.1868860.

[Pirovano04]   A. Pirovano, A. L. Lacaita, F. Pellizzer, S. A. Kostylev, A. Benvenuti and R. Bez, <u>Low-field amorphous state resistance and threshold voltage drift in chalcogenide materials</u>, *IEEE Trans. Electron. Devices* **51** (2004) 714-719, doi: 10.1109/TED.2004.825805.

[Potzger09] K. Potzger, and S. Zhou, <u>Non-DMS related ferromagnetism in transition metal doped zinc oxide</u>, *Phys. Status Solidi B* **246** (2009) 1147-1167, doi: 10.1002/pssb.200844272.

[Schuenemann00]   V. Schünemann, H. Winkler, <u>Structure and dynamics of biomolecules studied by Mössbauer spectroscopy</u>, *Rep. Prog. Phys.* **63** (2000) 263–353, doi: 10.1088/0034-4885/63/3/202.

[Seeger68]   A. Seeger and K. P. Chik, <u>Diffusion Mechanisms and Point Defects in Silicon and Germanium</u>, *Phys. Status Solidi B* **29** (1968) 455-542, doi: 10.1002/pssb.19680290202.

[Soares73]   J. C. Soares, K. Krien, A. G. Bibiloni, K. Freitag and R. Vianden, <u>Determination of the quadrupole splitting of the first excited state of ^{119}Sn in β-tin by the $e^- - \gamma$ TDPAC technique</u>, *Phys. Lett. A*, **45** (1973) 465-466, doi:10.1016/0375-9601(73)90710-X.

[Song07]   W. D. Song, L. P. Shi, X. S. Miao and T. C. Chong, <u>Phase change behaviors of Sn-doped Ge–Sb–Te material</u>, *Appl. Phys. Lett.* **90** (2007) 091904, doi:10.1063/1.2475390.

[Suezawa08]M. Suezawa and I. Yonenaga, <u>On the Extended Point Defect Model in Si Crystals at High Temperature</u>, *Jpn. J. Appl. Phys.* **47** (2008) 7117–7118, doi: 10.1143/JJAP.47.7117.

[Ye09]   H. B. Ye, J. F. Kong, W. Pan, W. Z. Shen, B. Wang, <u>Multi-carrier transport properties in p-type ZnO thin films</u>, *Solid State Comm.* **149** (2009) 1628-1632, doi: 10.1016/j.ssc.2009.06.030.

[Yoon07]   S. M. Yoon, K. J. Choi, N. Y. Lee, S. Y. Lee, Y. S. Park and B. G. Yu, <u>Nanoscale Observations on the Degradation Phenomena of Phase-Change Nonvolatile Memory Devices Using $Ge_2Sb_2Te_5$</u>, *Jpn. J. Appl. Phys.* **46** (2007) L99-L102, doi: 10.1143/JJAP.46.L99.

[Wang04]   K. Wang, D. Wamwang, S.Ziegler, C. Steimer, M. J. Kang, S. Y. Choi and M. Wuttig, <u>Influence of Sn doping upon the phase change characteristics of $Ge_2Sb_2Te_5$</u>, *Phys. Stat. Sol. (a)* **201** (2004) 3087-3095, doi: 10.1002/pssa.200406885.

[Wang08]   Q. Wang, Q. Sun, G. Chen, Y. Kawazoe and P. Jena, <u>Vacancy-induced magnetism in ZnO thin films and nanowires</u>, *Phys. Rev. B* **77** (2008) 205411, doi: 10.1103/PhysRevB.77.205411.

[Wang09]   Q. Wang, Q. Sun, P. Jena, and Y. Kawazoe, <u>Magnetic properties of transition-metal-doped $Zn_{1−x}T_xO$ (T=Cr, Mn, Fe, Co, and Ni) thin films with and without</u>

intrinsic defects: A density functional study, *Phys. Rev. B* **79**, (2009) 115407, doi: 10.1103/PhysRevB.79.115407.

[Watkins91] G.D. Watkins, in: W. Schröter (Ed.), Materials Science and Technology, Vol. 4, VCH, Weinheim, 1991, p. 105.

[Watkins08] G. D. Watkins, The vacancy in silicon: Identical diffusion properties at cryogenic and elevated temperatures, *J. Appl. Phys.* **103** (2008) 106106, doi: 10.1063/1.2937198.

[Welnic05] W. Welnic, A. Pamungkas, R. Detemple, C. Steimer, S. Blügel, and M. Wuttig, Unravelling the interplay of local structure and physical properties in phase-change materials, *Nat. Mat.* **5** (2005) 56-62, doi: 10.1038/nmat1539

[Wertheim64] G. K. Wertheim, and J. P. Remeika, Mössbauer effect hyperfine structure of trivalent Fe57 in corundum, *Phys. Lett.* **10** (1964) 14-15, doi: 10.1016/0031-9163(64)90547-5.

[Weyer80a] G. Weyer, S. Damgaard, J. W. Petersen, J. Heinemeier, Mössbauer study of ^{119}Sn defects in silicon from ion implantations of radioactive^{119}In, *Hyp. Int.* **7** (1980) 449-453, doi: 10.1007/BF01021527.

[Weyer80b] G. Weyer, A. Nylandsted Larsen, N. E. Holm, H. L. Nielsen, Radiation defects in ion-implanted silicon. I. Mössbauer spectrsocopy of ^{119}Sn defect structures from implantation of radioactive antimony, *Phys. Rev. B* **21** (1980) 4939-4950, doi: 10.1103/PhysRevB.21.4939.

[Weyer80c] G. Weyer, S. Damgaard, J. W. Petersen, J. Heinemeier, Sn impurity defects in germanium from ion implantations of radioactive ^{119}In, *Phys. Lett.* **76A** (1980) 321-323, doi: 10.1016/0375-9601(80)90506-X.

[Weyer82] G. Weyer, S. Damgaard, J. W. Petersen, J. Heinemeier, Comparison of Impurity Defect Structures Formed By Ion Implantation In Amorphous and Crystalline Silicon, *Nucl. Instr. Meth.* **199** (1982) 441-444, doi: 10.1016/0167-5087(82)90250-2.

[Weyer03] G. Weyer, H. P. Gunnlaugsson, M. Dietrich, M. Fanciulli, K. Baruth-Ram, R. Sielemann and the ISOLDE collaboration. Creation and annealing of defect structures in silicon-based semiconductors during and after implantation at 77-500 K, *Nucl. Instr. Meth. B*, **206** (2003) 90-94, doi: 10.1016/S0168-583X(03)00688-8.

[Weyer07] G. Weyer, Defects in semiconductors-results from Mössbauer spectroscopy, *Hyp. Int.* **177** (2007) 1-13, doi: 10.1007/s10751-008-9607-y

[Wickman66] H. H. Wickman, and G. K. Wertheim, Mössbauer Hyperfine Spectra of Fe3+ in Corundum: Magnetic-and Crystal-Field Effects, *Phys. Rev. B* **148** (1966) 211-217, doi: 10.1103/PhysRev.148.211.

[Wickman66b] H. H. Wickman, M. P. Klein, and D. A. Shirley, Paramagnetic Hyperfine Structure and Relaxation Effects in Mössbauer Spectra: Fe^{57} in Ferrichrome A, *Phys. Rev.* **152** (1966) 345-357, doi: 10.1103/PhysRev.152.345.

[zhou09] S. Zhou, K. Potzger, Q. Xu, G. Talut, M. Lorenz, W. Skorupa, M. Helm, J. Fassbender, M. Grundmann, H. Schmidt, Ferromagnetic transition metal implanted ZnO: A diluted magnetic semiconductor? *Vacuum* **83**, S13 (2009), doi: 10.1016/j.vacuum.2009.01.030.

Appendix 1: Publications since 2000 based on Mössbauer data obtained at ISOLDE

T. E. Mølholt, R. Mantovan, H. P. Gunnlaugsson, K. Bharuth-Ram, M. Fanciulli, H. P. Gíslason, K. Johnston, Y. Kobayashi, G. Langouche, H. Masenda, D. Naidoo, S. Ólafsson, R. Sielemann, G. Weyer, <u>Temperature and dose dependence of defect complex formation with ion-implanted Mn/Fe in ZnO</u>, *Physica B* **404** (2009) 4820-4822, doi: 10.1016/j.physb.2009.08.187.

K. Bharuth-Ram, H. P. Gunnlaugsson, G. Weyer, R. Mantovan, D. Naidoo, R. Sielemann, M. Fanciulli, G. Langouche, S. Olafsson, Th. Aigne, ISOLDE Collaboration, <u>Mössbauer study of Fe in GaAs following ^{57}Mn$^+$ implantation</u>, *Hyp. Int.* **119** (2009) 115–120, doi: 10.1007/s10751-009-9961-4

H. P. Gunnlaugsson, G. Weyer, R. Mantovan, D. Naidoo, R. Sielemann, K. Bharuth-Ram, M. Fanciulli, K. Johnston, S. Olafsson, G. Langouche, <u>Isothermal defect annealing in semiconductors investigated by time-delayed Mössbauer spectroscopy: application to ZnO</u>, *Hyperfine Interact.* **188** (2009) 85–89, doi: 10.1007/s10751-008-9893-4

D. Naidoo, H. P. Gunnlaugsson, K. Bharuth-Ram, V. V. Naicker, G. Weyer, R. Sielemann, R. Mantovan, M. Fanciulli, the ISOLDE Collaboration, <u>^{57}Fe Mössbauer Investigations in P-Type Silicon Germanium Single Crystals</u>. Hyp. Int. **188** (2009) 11-17, doi: 10.1007/s10751-008-9880-9

H. P. Gunnlaugsson, C. Bender Koch, K. Bharuth-Ram, M. Dietrich, Ö. Helgason, M. B. Madsen, R. Mantovan, D. Naidoo, S. Steinthorsson, L. Vistisen, G. Weyer, <u>Disordered chromite in the Martian meteoriteAllan Hills 84001</u>, *Hyperfine Interact.* **186** (2008) 9–14, doi: 10.1007/s10751-008-9834-2

K. Bharuth-Ram, H. P. Gunnlaugsson, R. Mantovan, V. V. Naicker, D. Naidoo, R. Sielemann, G. Weyer, Th. Aigne, ISOLDE Collaboration, <u>Mössbauer study of Fe in 3C-SiC following ^{57}Mn implantation</u>, *Hyperfine Interact.* **184** (2008) 207–211, doi: 10.1007/s10751-008-9791-9

K. Bharuth-Ram, V. V. Naicker, D. Naidoo, H. P. Gunnlaugsson, R. Mantovan, G. Weyer, M. Dietrich, J. E. Butler, ISOLDE Collaboration, <u>Mössbauer study of ^{57}Fe in CVD diamond following ^{57}Mn implantation</u>, *Hyperfine Interact.* **179** (2007) 17–22, doi: 10.1007/s10751-008-9669-x

G. Weyer, H.P. Gunnlaugsson, R. Mantovan, D. Naidoo, K. Bharuth-Ram, M. Fanciulli, T. Agne. <u>Defect-related local magnetism at dilute Fe atoms in ion-implanted ZnO</u>. *J. Appl. Phys.* **102** (2007) 113915.

G. Weyer, <u>Defects in semiconductors—results from Mössbauer spectroscopy</u>, *Hyp. Int.* **177** (2007) 1-13, doi: 10.1007/s10751-008-9607-y

H. P. Gunnlaugsson, K. Bharuth-Ram, M. Dietrich, M. Fanciulli, H. Fynbo, G. Weyer, <u>Identification of substitutional and interstitial Fe in 6H-SiC</u>, *Hyp. Int.* **169** (2006) 1318-1323.

H. P. Gunnlaugsson, K. Bharuth-Ram, M. Dietrich, M. Fanciulli, H. Fynbo, G. Weyer, Formation of Fe$_i$-B pairs in silicon at high temperatures, *Hyp. Int.* **169** (2006) 1315-1318.

H. P. Gunnlaugsson, A simple model to extract hyperfine interaction distributions from Mössbauer spectra, *Hyp. Int.* **167** (2006) 851-854.

G. Weyer, H.P. Gunnlaugsson, K. Bharuth-Ram, M. Dietrich, R. Mantovan, V. Naicker, D. Naidoo, R. Sielemann, Acceleration of diffusional jumps of interstitial Fe with increasing Ge concentration in $Si_{1-x}Ge_x$ alloys observed by Mössbauer spectroscopy, *Hyp. Int.,* **158** (2005) 417-421.

G. Weyer, H. P. Gunnlaugsson, M. Dietrich, H. Fynbo, K. Bharuth-Ram, and the ISOLDE Collaboration, Mössbauer spectroscopy on Fe impurities in diamond, *The Europ. Phys. J. – Appl. Phys.,* **27** (2004) 317-320.

H. P. Gunnlaugsson, G. Weyer, M. Dietrich, M. Fanciulli, K. Bharuth-Ram, R. Sielemann, and the ISOLDE Collaboration, Mössbauer spectroscopy on Fe impurities in germanium, *Physica B,* **340-342** (2003) 537-540.

H. P. Gunnlaugsson, G. Weyer, N.E. Christensen, M. Dietrich, M. Fanciulli, K. Bharuth-Ram, R. Sielemann, A. Svane, and the ISOLDE Collaboration, On the kinetics of the formation of interstitial Fe-vacancy pairs at high temperatures, (2003) *Physica B,* **340-342** (2003) 532-536.

G. Weyer, H. P. Gunnlaugsson, M. Dietrich, M. Fanciulli, K. Baruth-Ram, R. Sielemann and the ISOLDE collaboration. Creation and annealing of defect structures in silicon-based semiconductors during and after implantation at 77-500 K, *Nucl. Instr. Meth. B,* **206** (2003) 90-94.

H. P. Gunnlaugsson, G. Weyer, M. Dietrich, the ISOLDE collaboration, M. Fanciulli, K. Bharuth-Ram and R. Sielemann, Charge state dependence of the diffusivity of interstitial Fe in silicon detected by Mössbauer spectroscopy, *Appl. Phys. Lett.,* **80**(15) (2002) 2657-2659.

H. P. Gunnlaugsson, M. Dietrich, M. Fanciulli, K. Baruth-Ram, R. Sielemann, G. Weyer and the ISOLDE collaboration. Detection of substitutional and interstitial Fe in silicon by Mössbauer Spectroscopy, *Phys. Scripta,* **T101** (2002) 82-85.

H. P. Gunnlaugsson, M. Fanciulli, M. Dietrich, K. Baruth-Ram, R. Sielemann, G. Weyer and the ISOLDE collaboration. ^{57}Fe Mössbauer study of radiation damage in ion implanted Si, SiGe and SiSn, *Nucl. Inst. Meth. B,* **168**(1-4) (2002) 55-60.

H. P. Gunnlaugsson, M. Dietrich, M. Fanciulli, K. Baruth-Ram, R. Sielemann, G. Weyer and the ISOLDE collaboration. Detection of diffusional jumps of interstitial Fe in silicon by Mössbauer Spectroscopy, *Physica B*, **308-310** (2001) 418-420.

Appendix 2: Presentations at conferences/meetings (since 2005)

Presenter	Where	Type	Title
H. P. Gunnlaugsson	Isolde Workshop 2009	Invited talk	Paramagnetic Fe defects in ZnO
R. Mantovan	ICM 2009	Poster	Defect Magnetism induced in ZnO by Na implantation
D. Naidoo	ICDS 2009	Oral	On vacancy diffusion in SiGe
K. Baruth-Ram	ICDS 2009	Poster	Temperature and dose dependence of defect complex formation with ion-implanted Mn/Fe in ZnO
H. P. Gunnlaugsson	NSM 2009	Oral	On vacancy diffusion in SiGe
T. E. Molholt	NSM 2009	Oral	Lattice location and Diffusivity of interstitial Fe in MgO
R. Mantovan	ISOLDE Workshop 2008	Oral	Mössbauer studies of dilute magnetic semiconductors (IS-443)
G. Weyer	HFI 2007	Invited talk	Defects in semiconductors - results from Mössbauer spectroscopy
G. Langouche	ICDS 2007	Poster	High temperature 57Fe Mössbauer Spectroscopy of Magnetic Defects in ZnO
H. P. Gunnlaugsson	ICAME 2007	Oral	Isothermal defect annealing in semiconductors investigated by time-delayed Mössbauer spectroscopy: application to ZnO
H. P. Gunnlaugsson	ICAME 2007	Oral	Mössbauer spectroscopy of Fe in group III-V cubic semiconductors
H. P. Gunnlaugsson	ICAME 2007	Oral	Disordered chromite in the Martian meteorite Allan Hills 84001
D. Naidoo	ICAME 2007	Poster	^{57}Fe Mössbauer Investigations in P-Type Silicon Germanium Single Crystals
K. Baruth-Ram	ICAME 2007	Poster	Mössbauer study of Fe in 3C-SiC following ^{57}Mn implantation
H. P. Gunnlaugsson	Seeheim 2006	Invited talk	Application of radioactive ^{57}Mn^{+} ion beams for ^{57}Fe Mossbauer studies of semiconductors
H. P. Gunnlaugsson	ICAME 2005	Poster	Formation of Interstitial Fe – B Pairs at high temperatures
H. P. Gunnlaugsson	ICAME 2005	Poster	Identification of Substitutional and Interstitial Fe in 6H-SiC
H. P. Gunnlaugsson	ICAME 2005	Poster	A Simple Model to Extract Hyperfine Interaction Distributions From Mössbauer Spectra

Appendix 3: The [57]Mn Mössbauer collaboration at ISOLDE/CERN.

The team that internally called themselves "The [57]Mn Mössbauer collaboration at ISOLDE/CERN" has grown significantly in recent years. With 15 members directly involved in the Mössbauer measurements, thereof 7 with the expertise of running the equipment we will be able to make use of more number of beams, expanding considerably on the amount of physics that can be addressed. The list below contains the members and most important collaborating partners with respect of the current proposal.

Country/Institutions	Members	Facilities
Denmark, Department of Physics and astronomy, Aarhus University.	H. P. Gunnlaugsson, G. Weyer	Mössbauer Lab., MBE growth of Si/SiO_2 structures (A. N. Larsen), theoretical calculations of Mössbauer hyperfine parameters (A. Svane).
Iceland, Science Institute, University of Iceland.	S. Ólafsson, H. P. Gíslason, T. E. Mølholt (PhD student)	Mössbauer Lab., Sputtering growth of various samples, with various types of characterization techniques.
Italy, Laboratorio Nazionale MDM CNR-INFM, Milano; Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Milano	R. Manotvan, M. Fanciulli	Mössbauer Lab. Growth of samples (ALD) and various characterization techniques. EPR specialists.
South Africa, School of Physics, University of the Witwatersrand; University of KwaZulu-Natal, Durban; iThemba LABS, Somerset West.	D. Naidoo, K. Bharuth-Ram, W. B. Dlamini (PhD student), H. Masenda (PhD student), NN (PhD student)	Mössbauer Labs., Specialists in Nuclear Methods in Solid State Physics.
Belgium, Instituut voor Kern-en Stralings fysika, University of Leuven.	G. Langouche, S. Decoster (emission channeling)	Mössbauer Lab., Specialist in Mössbauer spectroscopy (GL). SD is our contact person regarding emission channelling experiments.
Germany, Helmholtz Forschungszentrum, Berlin.	R. Sielemann	Mössbauer Lab., Specialist in Mössbauer spectroscopy.
Switzerland, EP Division, CERN	K. Johnston	Radioactive Laboratory, equipment for annealing and off-line Mössbauer measurements.
Portugal, Departamento Física, Instituto Tecnológico e Nuclear	J. G. Correia, J. P. Araújo, M. B. Barbosa, A. L. Lopes (PAC)	Contact persons regarding PAC experiments and experiments overlapping

(ITN), Sacavém; IFIMUP, Porto; Centro de Fisica Nuclear da Universidade de Lisboa (CFNUL), Lisboa		with the IS481 experiment physics.
Japan, The Institute of Physical and Chemical Research (RIKEN), Wako; Shizuoka Institute of Science and Technology.	Y. Yoshida, Y. Kobayashi	Mössbauer Lab., complimentary GeV implantation of ^{57}Mn.