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Proposal

Mn and Fe impurities in $Si_{1-x}Ge_x$ alloys

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Summary

Following our investigations of Mn and Fe impurities in elemental semiconductors and in silicon in particular by means of on-line ^{57}Fe Mössbauer spectroscopy, utilizing radioactive $^{57}Mn^{+}$ ion beams at ISOLDE, we propose to extend these studies to bulk and epitaxially-grown $Si_{1-x}Ge_x$ alloys. In these materials, although already successfully employed in electronic devices, little is known about point defects and important harmful 3d impurities. The experiments aim to determine a variety of fundamental properties: The lattice location of ion-implanted Mn/Fe, the electronic and vibrational properties of dilute Fe impurities in different lattice sites, the charge-state and composition dependence of the diffusivity of interstitial Fe on an atomic scale, the reactions and formation of complexes with lattice defects created by the ^{57}Mn implantation or by the recoil effect in the nuclear decay to the Mössbauer state of ^{57m}Fe. Feasibility studies in 2003 indicate that these aims can be achieved; we ask for 8 shifts of $^{57}Mn^{+}$ ion beam.

1. Introduction

Fe and other 3d impurities in silicon, identified as the most harmful metal impurities in device technology [1], unintentionally incorporated during crystal growth or subsequent fabrication processes, have been the subject of dedicated research since more than 40 years. Recent reviews on the physics of Fe and its detrimental effects in devices as well as on (expensive) present strategies for their suppression (surface concentrations < $10^{12}/cm^2$) give more than 1000 references [2]. Most of these are concerned with interstitial Fe; the importance of (much more stable) substitutional Fe, in particular in ion-implanted material and highly-doped, n^+-type material, has been realized only recently and hardly more than some ten investigations have been reported [see introduction in ref. 1 and refs. 3-6]. The demand for lower contamination levels in future silicon-based devices with ever shrinking dimensions and consequently higher (ion-implanted) doping levels is likely to run into substitutional 3d impurities. It is evident from the similar bulk-crystal or epitaxial growth techniques of $Si_{1-x}Ge_x$ on silicon surfaces that 3d elements will play a likewise important role in these materials. More excitingly, first investigations of point defects and impurities (among them Fe) in such materials show the possibility to utilize SiGe as an "extended laboratory" [7], where further insight – also into the physics in pure silicon – can be gained by the ability to control, e.g. the band gap energy and the lattice-defect or impurity mobility by alloying or electronic effects. It is along such lines that we intend to enlarge the basis for a more profound understanding of the physics of Fe in group-IV elements in general and in $Si_{1-x}Ge_x$ in particular. The proposal is structured in the following way. In section 2 we briefly report on recent, partially unpublished results for Mn/Fe impurities in elemental group-IV semiconductors as well as on preliminary results for $Si_{1-x}Ge_x$ from the beam time in 2003. Section 3 gives the detailed program envisaged in this proposal and finally in section 4 we report on our technical abilities for such studies and give a beam time estimate.

2. Mn/Fe impurities in silicon and other elemental group-IV semiconductors

For single ion implantations (< $10^{12}/cm^2$) into silicon a major annealing stage at 300-400 K is known. Implantations or annealing above these temperatures of ^{57}Mn ($T_{1/2}$ = 1.5 min) leads to a predominant substitutional incorporation [6,9]. Location on or close to

substitutional sites has also been observed by emission channeling for other transition metals [8]. However, in the ^{57}Mn β^--decay to the 14 keV Mössbauer state of ^{57m}Fe recoil energies up to 84 eV are imparted on the daughter atoms, expelling most of them into tetrahedral interstitial sites. Thus the electronic configurations and impurity lattice vibrations, characterized by an impurity Debye temperature, have been determined for Fe on the two lattice sites [5, 6].

Implantations at > 500 K reveal the instability of Fe_I on interstitial sites, i.e. diffusional jumps during the lifetime of the Mössbauer state (140 ns) lead to a line broadening, which is directly proportional to the diffusivity. For interstitial $Fe_I^{+/0}$ thus determined diffusivities on an atomic scale were pronouncedly different for the two charge states [9, 10], in accordance with macroscopic measurements of only one group [11], settling a long-lasting dispute [2]. At temperatures > 600 K, a Fe_I-V complex is formed with the vacancy created in the recoil process. The complex is stable – as is substitutional Fe – during 140 ns up to > 1050 K [9, 12]. Ab-initio full-potential linear-muffin-tin-orbital total energy calculations show this to be a metastable pair, with interstitial Fe_I displaced along <-1-1-1> axes towards the vacancy; calculated hyperfine parameters are in very good agreement with the experimental results for the pair as is also the case for substitutional and interstitial Fe [12]. While the structure and stability of the pair is in agreement with recent EPR results [13], the formation process is apparently different. At about 300 K [13] the pair is formed by the mobility of vacancies, i.e. with diffusion activation energies of 0.2 - 0.45 eV for differently charged vacancies (created in e^--irradiations), whereas the activation energy is pronouncedly larger at 600-800 K, 0.6-0.9 eV, and agrees well with that for the diffusion of interstitial Fe_I [11]; i.e. no vacancy mobility is indicated. This raises the question whether the nature of the vacancy in silicon changes at high temperatures and the diffusivity decreases as proposed more than 30 years ago [14] but where other independent experimental evidence has only been obtained recently [15]. It is noteworthy that in analogous experiments in germanium the Fe_I-V pair is formed at 350 K in accordance with the mobility of the vacancy [16]. Evidently, following the formation of this pair as a function of x in $Si_{1-x}Ge_x$ alloys appears rewarding and might shed further light on the properties of vacancies, known to mediate the self-diffusion in germanium, whereas self-interstitials have been involved

also to explain self-diffusion in silicon [14]. A switchover from one to the other mechanism has been proposed to occur in $Si_{1-x}Ge_x$ at x = 0.5-0.6 [17, 18], whereas the vacancy nature changes already for smaller x values [7].

The mechanism of damage creation within ps in ion implantations at < 300 K in silicon and its annealing has been treated extensively by molecular dynamics computer simulations, e.g. ref. 19 and refs. cited there, whereas direct experimental information is difficult to obtain, mostly the resulting final structures have been studied. The combination of results from in-beam implantations of $^{57m}Fe^+$ ions, Coulomb-excited in the Mössbauer state [20], and our $^{57}Mn^+$ implantations, where the annealing occurs on, respectively, time scales of 10^{-7} and 10^2 s, gives some insight into the evolution of the damage cascades on such time scales [6, 21]. In both cases the fate of the probe atoms is followed as a function of implantation/annealing temperature. At < 77 K the majority of probe atoms is incorporated in defect sites of non-cubic symmetry, characterized by a narrow, correlated distribution in quadrupole interactions and electron densities, and a minor fraction in (cubic) tetrahedral interstitial sites. Partial defect annealing occurs at 100-200 K on a time scale < 100 ns, i.e. it is most likely related to a temperature dependence of the damage creation mechanism or its dynamic annealing. The major annealing stage at 300-400 K and 800 K on time scales of, respectively, 10^2 and 10^{-7}s is consistent with the formation and annealing of “amorphous” pockets [19], indicating that this defect type is dominantly created initially in ion implantations. Implantations of $^{57}Mn^+$ into amorphous silicon confirmed the similarity of the atomic surroundings [21]. However, in both cases, the recoil effect in the nuclear decay does not give rise to any new atomic configuration, thus locally similar structures are created also at very low energy. This is consistent with the formation of a defect, named “bond defect” [19, 22], consisting of an IV pair complex, if one of the Si atoms is replaced by a Fe atoms. The bond defect is predicted theoretically to have a very low formation energy and all atoms are four-fold coordinated. This is consistent with a Fe Debye temperature in the defect site, which is the same as that on substitutional sites in crystalline silicon, twice as large as for interstitial sites [6, 21]. Very similar Fe defects dominate in low temperature implantations in all group-IV elements, the quadrupole splittings and isomer shifts scale

nicely with the bond-length of the material as also observed for substitutional and interstitial Fe [23]. The formation of “amorphous” pockets is proposed to occurs by agglomeration of bond defects [19], i.e. the involved atoms would have slightly different atomic configurations, consistent with the observed distribution in the Fe isomer shifts and quadrupole splittings. This defect type, which apparently is not electrically active, and “amorphous” pockets have been involved in the interpretation of results from Rutherford backscattering/channeling and TEM studies in ion-implanted silicon [19, 24]. However, to the best of our knowledge, in particular no other experimental information on the atomic structure of such defect types exists.

2. Proposed experiments with ^{57}Mn/^{57}Fe in $Si_{1-x}Ge_x$ random alloys

The kinematic factors for binary collisions of implanted ^{57}Mn atoms with Si, Ge and Sn target atoms are favorable for replacement collisions with Ge, whereas these are similarly unlikely for Si and Sn. Accordingly, implantations at temperature below the main annealing stage into Si, SiGe and SiSn alloys [6] result in negligible substitutional fractions for Si and SiSn, while larger fractions are observed in Ge and SiGe alloys. The substitutional fractions in SiGe alloys can thus be tuned by the Ge concentrations. More importantly, this applies also for the low recoil energies of the ^{57m}Fe daughter atoms [6]. Additionally, probably by dynamic annealing on a ps time scale, in damage cascades a strong influence of chemical potentials on final lattice sites is well-known also [25]. On the other hand, these should not be important at low energies. By systematic studies of Mn/Fe lattice site distributions in $Si_{1-x}Ge_x$ alloys more detailed knowledge on high and low energy effects appears obtainable. The main purpose of these studies, however, is to characterize further the nature of the “amorphous” pockets and/or bond defects and their annealing behaviour by tracing the evolution as a function of composition and temperature.

In implantations at higher temperatures, above the main annealing stage, the dependence of the Fe_I diffusivity and the formation of Fe_I-vacancy complexes as a function of x are the main issues. Recent investigations of Fe_I^+ in $Si_{1-x}Ge_x$ up to x = 0.095 showed no change in the macroscopic diffusivity, however, the authors point out that this could be different on an atomic scale [26]. The reason lies in the Fe_I diffusion mechanism, which

is purely interstitial with the hexagonal interstitial site as the saddle point [27]. For low values of x sufficient “Ge-free” pathways hardly affect the long-range diffusion. Furthermore, the $Fe_I^{0/+}$ donor level was found to shift towards the valence band linearly with x and is predicted to merge with it at x = 0.25 [26]. Preliminary results from our beam time in 2003 show an increase of the Fe_I^0 diffusivity for x = 0.2, whereas in pure Ge it is most likely lower than in Si [16]. Thus the mechanism should change somewhere in between and also alloying effects may differ for the $Fe_I^{0/+}$ diffusivities as a function of x. Accurate measurements for Fe_I^0 in particular could therefore contribute to a more profound understanding of the diffusion mechanism and to disentangle the interplay of electronic and alloying effects.

Similar considerations apply to the formation of Fe_I-V pairs. Here, in electron irradiations upon increasing x, the formation of Ge-V pairs has been shown to compete with e.g. the formation of divacancies or E-centers, donor-vacancy pairs, which also show an enhanced stability [7]. Preliminary results for the formation of Fe_I-V pairs do not indicate any pronounced influence for x = 0.2, consistent with a formation due to Fe_I mobility. For x = 0.8 the pair forms at lower temperature and apparently anneals at 900 K, i.e. a full cycle from the creation of a distant Fe_I - -V pair through the formation of a close Fe_I-V pair and the final annihilation, resulting in substitutional Fe, can be followed. More data are needed to determine accurate hyperfine parameters and activation energies.

3. Technical requirements and beam time request

For low-temperature implantations and measurements we will apply existing liquid-nitrogen and helium-flow cryostats, developed for on-line Mössbauer spectroscopy. These have 14 and 6 crystal positions, respectively, thus change of samples does not necessitate to break the vacuum. For high-temperature implantations we will utilize an upgraded chamber, where four samples can be heated individually by a halogen lamp up to 1100 K. In all cases resonance detectors are employed, equipped with stainless steel or α-Fe absorbers enriched to ≥ 95% in ^{57}Fe. These are mounted on an electromagnetic drive system outside the chambers. Data are taken in multiscaling mode with a PC. Data analysis is performed likewise on PCs with the VINDA software, specially developed for

simultaneous analysis of series of spectra, e.g. as a function of temperature. No CERN computing support is needed.
$Si_{1-x}Ge_x$ alloys grown epitaxially on silicon in Aarhus up to x = 0.2 exist as well as bulk crystals with larger x values.

Beam time request: We ask for two runs of 3-5 shifts with laser-ionised $^{57}Mn^+$ at the GLM beam line, in total 8 shifts. The required minimum intensity is $5 \cdot 10^7$ ions/s.

References:

[1] http://public.itrs.net/
[2] A.A. Istratov et al., Appl. Phys. A 69 (1999) 13 and ibid. A 70 (2000) 489
[3] D. Gilles et al., Phys. Rev. B 41 (1990) 5770
[4] G. Langouche, Hyp. Int. 72 (1992) 217
[5] G. Weyer et al., Physica B 273-274 (1990) 363
[6] H.P. Gunnlaugsson et al., Nucl. Instr. Meth. B 186 (2002) 55
[7] A. Mesli and A. Nylandsted Larsen, Nucl. Instr. Meth. B 211 (2003) 80
[8] U. Wahl, Hyp. Int. 129 (2000) 349
[9] H.P. Gunnlaugsson et al., Physica Scripta T 101 (2002) 82
[10] H.P. Gunnlaugsson et al., Appl. Phys. Lett. 80 (2002) 82
[11] T. Heiser an A. Mesli, Phys. Rev. Lett. 68 (1992) 978
[12] H.P. Gunnlaugsson et al, Physica B, in press
[13] T. Mechedlize and M. Suezawa, Jpn. J. Appl. Phys. 41 (2002) 7288
[14] A. Seeger and K.P. Chik, phys. stat. sol. 29 (1968) 455
[15] H. Bracht et al., to be publ.
[16] H.P. Gunnlaugsson, Physica B, in press
[17] N.R. Zangenberg et al., Phys. Rev. Lett. 87 (2001) 125901
[18] A. Strohm et al., Z. f. Metallk. 93 (2002) 737
[19] L.A. Marques et al., Phys. Rev. Lett. 91 (2003) 135504
[20] P. Schwalbach et al., Phys. Rev. Lett. 64 (1990) 1274

[21] G. Weyer et al., Nucl. Instr. Meth. B 206 (2003) 90

[22] S. Goedecker et al., Phys. Rev. Lett. 88 (2002) 235501

[23] G. Weyer et al., Eur. J. Appl. Phys., to be publ.

[24] G. Hobler and G. Otto, Mat. Sci. in Semicond. Processing 6 (2003) 1

[25] G. Weyer et al., Phys. Rev. Lett. 44 (1980) 15

[26] A. Mesli et al., Phys. Rev. B 66 (2002) 045206

[27] Y. Kamon et al., Physica B 308-310 (2001) 391