

Local Structure of Iron Implanted in Indium Phosphide

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1. Introduction

The intentional inclusion of foreign atoms in semiconductors is a common method to tailor their physical properties. When Iron atoms are substitutionally located within the InP lattice they alter the electrical properties of the host in a desirable way. Substitutional Fe^{2+} gives rise to a deep acceptor level in the mid-gap region of the InP band structure [1]; in fact, Fe is routinely used in optoelectronic device technology to compensate unintentional n-doping of InP in order to produce semi-insulating behavior. One of the problems in the use of Fe in InP is its rather low solubility: the maximum concentration of Fe^{2+} centers (before precipitation occurs) is 10^{17} atoms cm^{-3} . Recently, a new non-equilibrium method based on ion-implantation has been shown [2, 3, 6] to be able to achieve active Fe concentrations in the order of 10^{19} atoms cm^{-3} ; in this method implantation is performed while heating the sample, thus reducing sample damage and defect production. Post-implantation annealing in a phosphine flux is used to further re-order the host crystal and activate the Fe^{2+} centers.

While it is clear that non-equilibrium ion implantation allows significantly higher levels of active Fe to be obtained, open questions regarding the structural location of Fe in the InP host exist. The most important one is that electrical measurements show that only a fraction ($\sim 10\%$) of the implanted Fe is active; while it is possible to formulate hypotheses on the nature of the inactive Fe (metallic Fe, Fe oxide, Fe-P precipitate [4], interstitial Fe) no structural data is available in the literature.

X-ray absorption fine structure spectroscopy (XAFS) with synchrotron radiation is a powerful tool to study the local structure of atoms implanted in semiconductors (for a recent example see [5]). The chemical selectivity allows to extract the structural signal involving only the photoexcited atom, the local nature of the XAFS effect guarantees a high sensitivity to the local atomic environment and, finally, using fluorescence detection relatively low atomic concentrations can be probed. The development and availability of third-generation x-ray sources allows to significantly extend XAFS studies of implanted atoms. In fact, the high brilliance makes it possible to obtain high quality data on dilute species.

We have performed XAFS measurements on Fe implanted InP with the aim of providing a local structural characterization and thus clarifying the origin of the low fraction of active Fe sites. From an experimental point of view these measurements are rather challenging due to the low level of Fe ($\sim 10^{15}$ atoms cm^{-2}) and to the ubiquitous presence of Fe in the experimental chamber. Results obtained with complementary techniques (SIMS and PIXE) will be briefly mentioned. A preliminary report on this data has been recently published [6].

2. Experiment

Czochralski n-doped (001) InP wafers were used as implantation substrates, both Sn and S doped, with background electron concentration ranging from 3.7×10^{17} up to 1×10^{19} cm^{-3} . Samples were placed on a substrate holder kept at a temperature $T = 220$ °C during implantation. Single energy Fe implants were performed either at 2 MeV and 300 keV with a dose of 2×10^{15} cm^{-2} or at 350 keV with a dose of 3×10^{15} cm^{-3} . Annealing was carried out at a temperature of $T = 600$ or 700 °C for 1 hour and 30 minutes in a MOCVD reactor with a phosphine flux in order to prevent surface decomposition due to P evaporation. The most important sample characteristics are listed in Table 1.

SIMS depth profiles were obtained with a CAMECA IMS4f instrument, using a 5.5 keV oxygen primary beam and detecting $^{56}\text{Fe}^+$ secondary ions. The profiles of the high energy

implanted samples show a projected range R_p around 1.2 μm and a Fe maximum penetration depth of about 2 μm ; for the low energy implants instead R_p has a value between 0.2 and 0.3 μm and the penetration depth is at most 1 μm . Fe peak concentrations are 10^{19} atoms cm^{-3} for the 2 MeV implants and between 10^{19} and 10^{20} atoms cm^{-3} for the low energy ones. Fe lattice location by PIXE-channeling was carried out with a 1.85 MeV H^+ beam detecting the Fe K_α line at 6.4 keV with a Si(Li) detector. Angular scans across the major axial and planar crystallographic directions were performed. Proton backscattering spectra were recorded in parallel with each PIXE spectrum in order to compare the Fe and In angular yield; the In signal was integrated from the surface over a thickness containing about 90 % of the total Fe content. PIXE-channeling measurements performed on as-implanted samples show that a high fraction of iron atoms (from 30% in 9hda to 80% in 11h0) is located in tetrahedral symmetry sites of the InP lattice (substitutional and interstitial). This tetrahedral fraction is strongly reduced to values lower than the PIXE detection limit upon the annealing treatments. Further details on the PIXE-channeling analysis are given in ref.[6].

XAFS experiments at the Fe K-edge were performed at the ‘‘GILDA’’ (BM 8) beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A dynamically sagittally focussing Si(311) monochromator [7] was used and harmonics were rejected using a pair of Pd-coated grazing incidence mirrors and by detuning the crystals. The Fe absorption coefficient was monitored by measuring the intensity of the Fe K_α fluorescence, using a 13-element hyper-pure Ge detector equipped with digital electronics and a 1 μs peaking time. Count rates were of the order of a few 1000 counts per second at most. In order to reduce experimental artifacts (‘‘glitches’’) due to the single crystal nature of the substrate the samples were mounted on a vibrating sample holder [8].

Sample number	Sample code	Implantation Energy	Dose (at/cm ²)	Annealing	Coordination Number	σ^2 (10 ⁻³ Å ²)	R (Å)
1	7ha0	2 MeV	2×10^{15}	No	4.85 ± 0.62	9.9 ± 3.1	2.338 ± 0.017
2	7hc1	2 MeV	2×10^{15}	700 °C, 1h 30 min	5.91 ± 0.67	8.4 ± 2.7	2.358 ± 0.014
3	9hda	350 keV	3×10^{15}	No	4.25 ± 0.39	6.9 ± 2.3	2.346 ± 0.012
4	9hd2	350 keV	3×10^{15}	600 °C, 1h 30 min	5.64 ± 0.73	7.4 ± 3.2	2.338 ± 0.017
5	11h0	300 keV	2×10^{15}	No	3.58 ± 0.36	4.5 ± 2.3	2.386 ± 0.013
6	11ha1	300 keV	2×10^{15}	600 °C, 1h 30 min	5.75 ± 0.86	8.1 ± 3.6	2.375 ± 0.019

Table 1: Sample characteristics and results of the fitting procedure for the Fe – P first shell.

3. Results

XAFS data were quantitatively analyzed with the AUTOBK and FEFFIT programs [9] using theoretical phase signals generated by FEFF 8.0 [10]. Raw absorption data were background-subtracted using the AUTOBK routine. In Fig. 1 we report the raw, background subtracted, XAFS data. Despite the low concentration the spectra are of sufficient quality to obtain first shell information; the quality of spectra for samples 1 and 2 is slightly worse

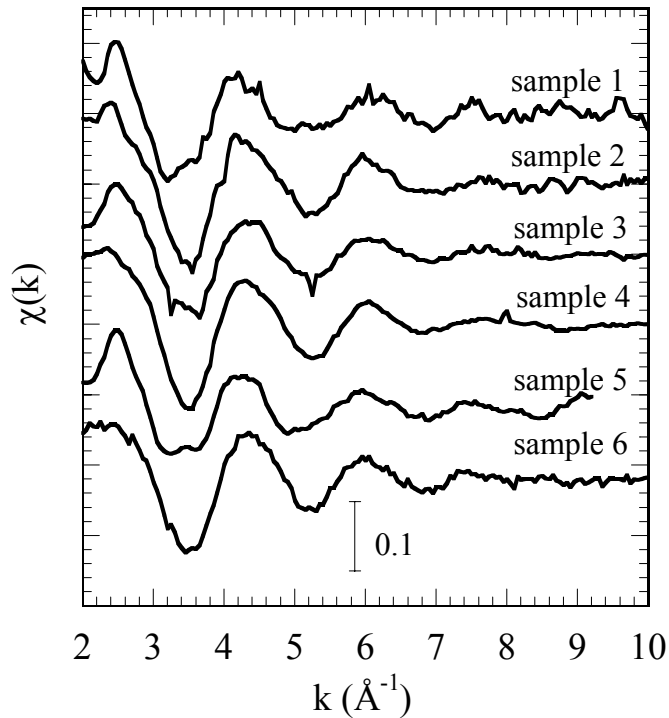


Figure 1: Raw, background subtracted, XAFS data.

compared to the others due to the lower dose and to the less superficial Fe distribution. Qualitative inspection shows only a single frequency signal to be present; the envelope of oscillations decreases rapidly as a function of the wavevector k , suggesting bonding with a low Z element.

The lineshape and position of the near – edge region of the X-ray absorption coefficient of these samples (see XANES spectra in Fig. 2) was clearly different from that of bulk BCC Fe or of any of the iron oxides, while some similarities can be found with the spectra of Fe – P stoichiometric compounds. Therefore, implanted Fe is never present in metallic or oxide form. This observation and the previously described qualitative analysis of the XAFS data suggest the Fe is instead locally bonded to P atoms.

XAFS spectra were quantitatively analysed using *ab-initio* phase shifts generated by FEFF 8.0. In order to generate theoretical signals a cluster consisting of an Fe substitutional atom in the InP lattice (with no lattice relaxation) was used. Fe and P form a series of compounds; of these, the 1 to 1 stoichiometry compound, FeP, has one of the simplest structures, with Fe being six-fold coordinated to P with interatomic distances in the range 2.24 to 2.35 Å . The theoretical signals generated by FEFF successfully reproduced an experimental spectrum of a FeP powder measured in the transmission mode. The value of the many-body amplitude reduction factor was obtained from these fits.

The spectra of the Fe implanted samples were fitted in the R-range 0.9 to 2.6 Å and in the k range 2.8 to 10 Å⁻¹, using a k^0 weight and a single Fe – P signal. The fitting parameters were the interatomic distance, the mean square relative displacement (σ^2), the coordination number (CN) and an energy origin shift; the many-body amplitude reduction factor was fixed to the value found from analysis of the FeP standard compound. The results of the quantitative analysis are reported in the last three columns of Table 1 (reported errors are purely statistical and correspond to 1σ in the fitted parameter) while in Fig. 3 we report the comparison between the filtered first shell contribution and the fit.

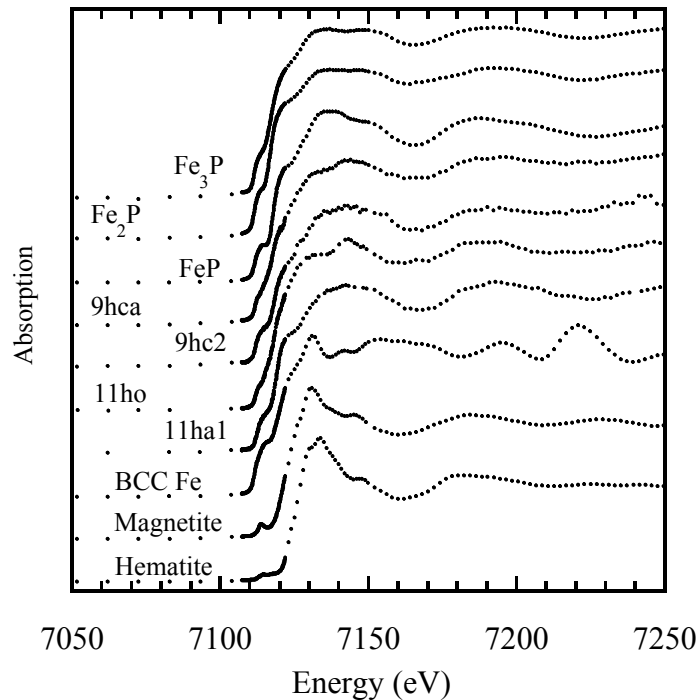


Fig. 2: XANES spectra of reference compounds and selected samples.

The reported data demonstrate that Fe is always bonded to P atoms. However, there are significant differences in the local structural parameters among the samples and in particular between the as – implanted and the annealed ones. The main difference is a systematic increase in the Fe – P CN upon annealing. This is especially clear in samples 3 to 6: with annealing the CN goes from a value close to 4 to a value close to 6. While it is difficult to propose a unique structural model and it is highly probable that in these sample Fe is present in a number of different local configurations the values for the CN suggest that in the as – implanted samples Fe is predominantly in a local configuration with a CN close to 4 (especially samples 3 and 5), and that annealing induces a transition to a CN close to 6. A CN equal to 4 would be found for a substitutional or an interstitial Fe in the InP lattice while a CN equal to 6 would be found in local structures similar to FeP or FeP₂. The absence of a structural signal beyond the first coordination shell indicates, in all cases, that the local surrounding of Fe is quite disordered beyond the first shell (i.e. it is never exclusively in an undistorted substitutional site) and/or that the spatial extent of the compound is extremely small. The values of the first shell σ^2 do not vary much (except for sample 5) and are constant at moderately high levels. The interatomic distances determined from the fit are close to Fe – P bond lengths in FeP or FeP₂, which range between 2.243 and 2.35 Å, and also to the sum of the covalent radii of Fe and P. Also in as-implanted samples the distances are significantly shorter than those of unrelaxed InP (2.541 Å): locally the InP lattice is strongly distorted if Fe substitutes In or if it is located in interstitial positions.

To summarise the experimental findings, we have evidence that in the as – implanted sample Fe is predominantly present in low CN sites, such as substitutional or interstitial sites, while in the annealed samples Fe is present in higher coordination number local structures, such as those found in some Fe – P compounds; in all cases the structures are not ordered beyond the first coordination shell. This is also in agreement with the PIXE-channeling results on the Fe lattice location. The annealing-induced formation of electrically – inactive FeP compounds

might very reasonably be at the origin of the limited electrical activation of Fe in the annealed samples.

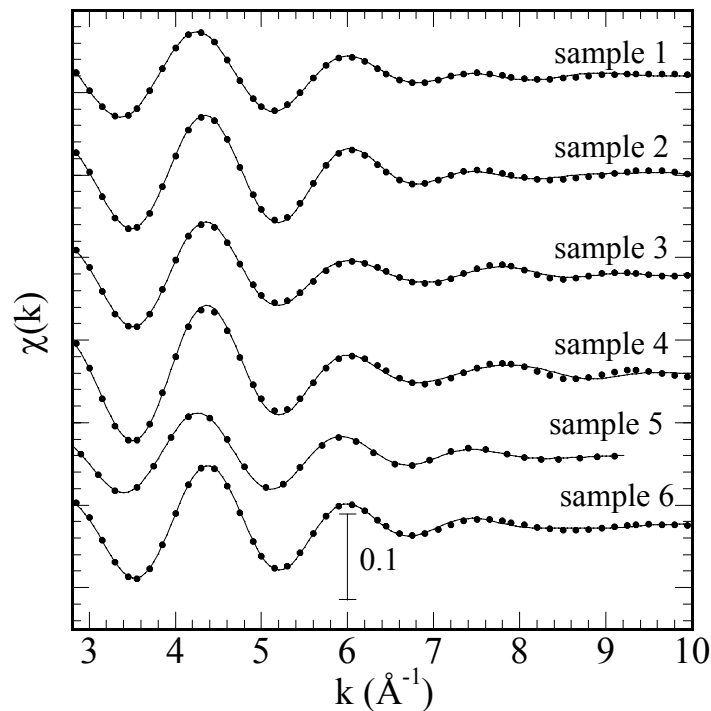


Figure 3: Comparison of the filtered first shell contribution and of the fit.

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Publications

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- 3) A.Gasparotto, T. Cesca, B. Fraboni, F. Boscherini, F. Priolo, G. Ciatto, F. D'Acapito, submitted to Phys. Rev. B.

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