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Conversion Electron Mössbauer Spectroscopic Studies of Ion Implanted Iron

Ion implantation is a method to influence surface properties of metals like corrosion or friction and wear behaviour. The implantation range has a thickness of some 100 nm. In this range structural changes like compound formation, crystallographic redistribution, and amorphisation can occur. The nature of those processes determines assentially the properties of the implantation product.

The physical question rises how the implanted ions are embedded in the host lattice? Mössbauer spectroscopy is a method which can contribute to the solution of this problem. Mössbauer effect gives informations on the location of atoms in the molecules and crystal lattices.

Two arrangements are possible:

Firstly, the implantation of the Mössbauer isotop in a matrix not containing a Mössbauer isotope itself followed by the study of the interaction between implanted and host atoms

and secondly, the implantation of any ions in a matrix containing a Mössbauer isotope. Then it is necessary to detect only those resonance events occurring in the implanted region. For transmission experiments this is nearly impossible and therefore this method is less accurate than the first but more attractive because of the great technical interest.

For instance, I mention the implantation of nitro-

gen in steel.

The conversion electron Mössbauer spectroscopy is a scattering technique and excludes the disadvantage of the second method nearly completely. It is very suitable for the study of iron or steel specimens.

Using this technique not the 14.4 keV-/-rays but the conversion and Auger electrons are detected. These electrons have a maximum energy of 7.3 keV. The Mössbauer signal can be obtained from a surface layer of about 300 nm. But the major part of the signal, namely 65 %, comes from the first 50 nm. This range is just interesting for ion implantation.

The experimental conditions are seen in Fig. 1. The Mössbauer measurements were carried out with a conventional spectrometer and a 100 mCi source Co-57 in Rh in a backscattering geometry. The samples were mounted on the backplate of a simple proportional counter; the Polish model LEK 2, through which helium with 5 % methan was allowed to flow. The gas glowrate was about 2 l/h. The counter voltage was 1400 V. The samples had a diameter of 40 mm and a thickness of 1 mm.

Implatations were carried out with different implantation devices being present at Rossendorf.

In a first series Mössbauer spectra of iron implanted with nitrogen in different implanters were studied. Implantation dose was $1.2 \cdot 10^{18}$ N/cm^2 and implantation voltage was 50 kV for all specimens, only the current density was varied between 5 and 32 μA/cm^2.

The Mössbauer spectra are seen in Fig. 2. The interpretation of spectra was carried out in comparison with /1/ where the implantation of iron with nitrogen is also studied. The spectra of non-implanted iron F0 and of three implanted iron targets are seen. Samples FN 8 and 9 were implanted with one implanter, sample FN 6 with another one. The current densities for FN 8 and 6 were the same and was higher for FN 9. The non-implanted iron produce the typical 6-line-pattern

of -iron. The spectrum of sample FN 8 shows both the sextet of -iron and an approximately central quadrupole doublet with a splitting of about 0.2 mm/s. This is due to a phase of composition around Fe_2N. This part of the spectrum is roughly identical with that measured by Longworth and Hartley. Only the intensity ratio between the doublet and the sextet in somewhat changed because the implanter does not possess any mass separation. The nitrogen molecule ions were not separated from the signale nitrogen ions. When the diatomic N_2^+ ion having energy of 50 keV strikes the sample surface it dissociates into two 25 keV N^+ ions. Therefore the nitrogen is deposited nearer at the surface than in the study of Longworth and Hartley. The range of compound formation seems to be narrower and the portion of -iron in the spectrum is increased.

The peak at 7.5 mm/s is related to iron oxide. Since there was no mass separation the oxygen could reach and oxidiethe sample surface. Probably the oxygen penetrated through the nitrogen pipe of the ion source into the acceleration chamber.

The spectrum of sample FN 6 is corresponding to that which Longworth and Hartley obtained by annealing the sample for one hour at 275°C. There are seen two sextets, one of -iron, another one of $-Fe_2N$.

The explantation for this difference is to be found in the different implantation technology. Sample FN 6 was implanted without interruptions and without special cooling. So it could warm up during irradiation. Sample FN 8 was implanted in intervals which allowed to cool during the implantation stops and it was mounted on a Large metal block.

Sample FN 9 was implanted in intervals too but with a high current density. Because of the stronger heating diffusion processes start and the nitrogen begins to migrate out of the investigated region. Besides the sextet of -iron and the doublet of Fe_2N in the spectrum an additional sextet

corresponding to -Fe_4N seen. The portion of iron oxide is higher than in the spectrum of sample FN 8.

The technical importance of nitrogen implantation in steel and iron is to be found in a possible decrease of mechanical wear. Implantation of phosphorus is supposed to prevent or to reduce corrosion.

For conversion electron Mössbauer spectroscopy is to note that implantations with the same voltage produce different range distributions for nitrogen and phosphorus. This fact can be seen in Fig. 3.

The distribution functions were calculated according in the theory of Lindhard, Scharff and Schiott /2/. It is seen that an implantation voltage between 100 and 200 kB is necessary for phosphorus to obtain a similar range distribution as for nitrogen with 50 kV. Specimens implanted with phosphorus at 50 or 100 kV should show a Mössbauer spectrum with a great portion produced by the layer behind the implanted range.

Electron mictroscopic studies on thin iron films have shown that a dose of $6 \cdot 10^{16}$ phosphorus ions/cm^2 is sufficient to amorphisize the implanted-range completely /3/. Mössbauer studies carried out on thick iron sheets could not confirm this result. A dose of $8 \cdot 10^{16}$ cm^{-2} is necesary in order to let appear a little singulet line in the spectrum of -iron lower doses are built in without disturbing the iron lattice visibly /Fig. 4/.

The portion of the central line reaches its maximum at $2 \cdot 10^{17}$ ions/cm^2 and does not further change with increasing implantation dose.

That line is the result of iron atoms without iron neighbours by reason of the high phosphorus doping. The portion of -iron in the spectra is roughly the same, it is caused by the volume behind the implanted layer. The central line could not be found at $1 \cdot 10^{17}$ cm^{-2} implantation.

In the spectra of specimens FP 10 and FP 11 a doublet additionally to the central line appears. This is due to iron clus-

ters.
In a further study the implantation energy was increased to 100 and 200 keV /Fig. 5/. Up to doses od 1 . 10^{17} ions/cm^2 the samples produce the 6-linepattern of -iron without other components. Only higher doses let it change. The Mössbauwer spectra of three phosphorus implanted iron disks are seen. The implantation doses were the same for all samples, 5 . 10^{17} cm^{-2}, but the implantation voltages were 50, 100, and 200 keV, respectively.

The spectra show distinctly the decreasing portion of -iron with increasing implantation voltage. This is due to the increasing penetration depth of the implanted phosphorus ions. Finally only electrons emitted from the implanted region were still emitted.
In all three spectra the central peak is seen again, in both lower the doublet too. In the spectrum of specimen FP 14 additional lines appear, moreover a general increanse of underground symmetrically to the middle point resulting from amorphisation of the great depth region is seen. So far as the experimental results.

In future it will be tryed to find out reason for the discrepancy between the studies on thin films and thick sheets. There are two parameters in study. Firstly, it is the sample temperature during implantation, because slight annealing is sufficient to allow the amorphous layer to recrystallize.

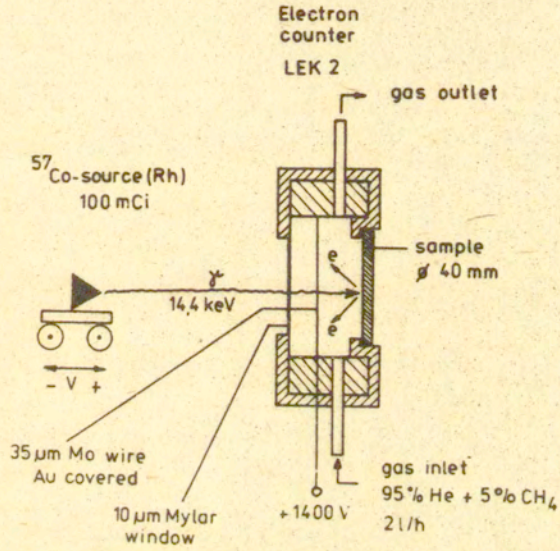
And secondly, it is the texture of the used iron sheets. It is supposed that a strong texture hinders amorphisation. Therefore Mössbauer measurements on samples without texture are planned.

References

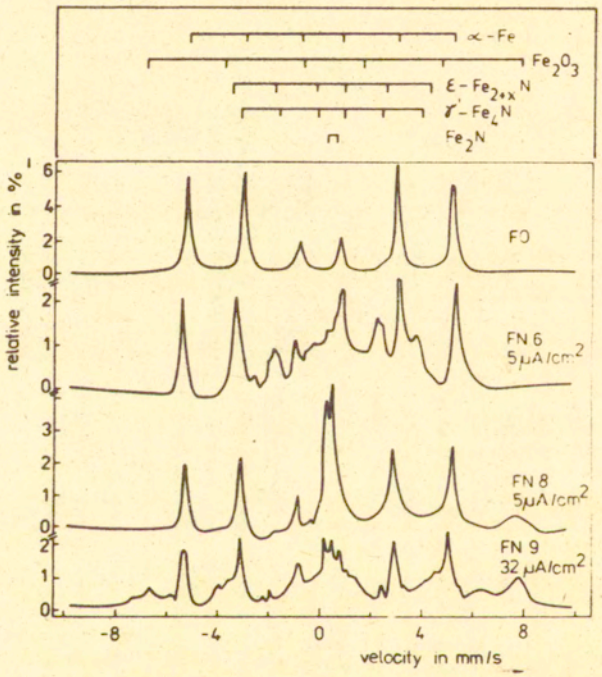
/1/ G.Longworth, N.E.W. Hartley, Thin Solid Films 48 /1978/ 95

/2/ J.Lindhard, M.Scharff, H.E.Schiott, Mat.Fys.Medd. 33 /1963/ 14

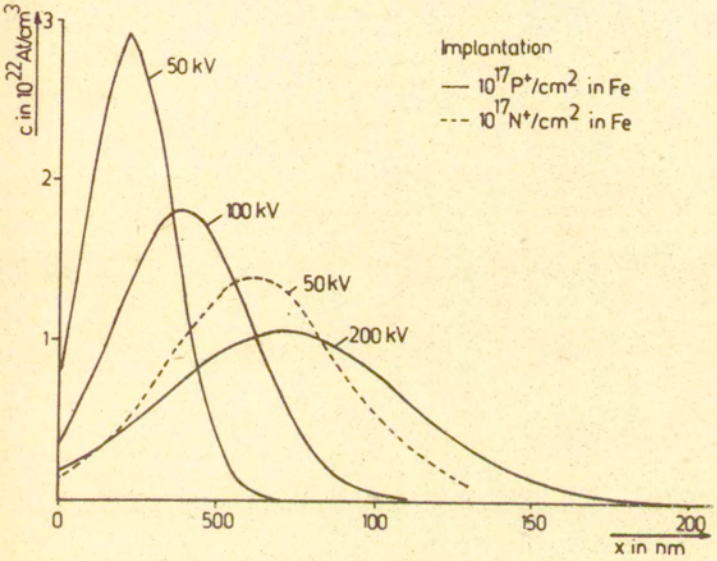
/3/ K.Rohmuth, A.Kolitsch, B.Rauschenbach, J.Non-Cryst. Solids 56 /1983/ 381



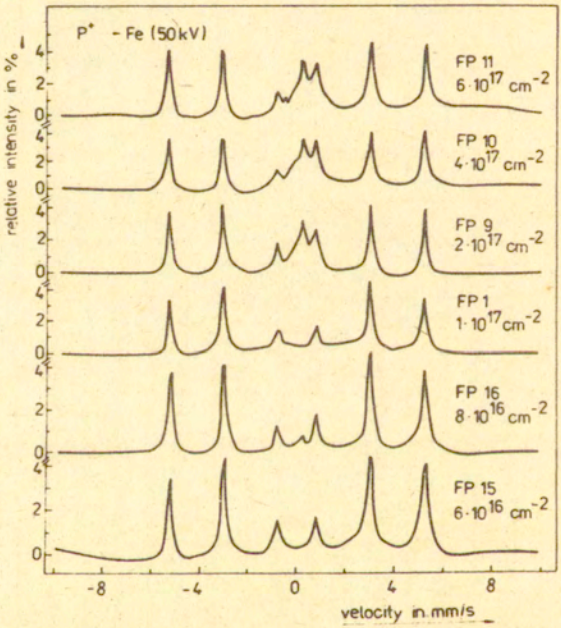
Rys. 1. Experimental setup for the conversion electron Mossbauer Sectroscopy



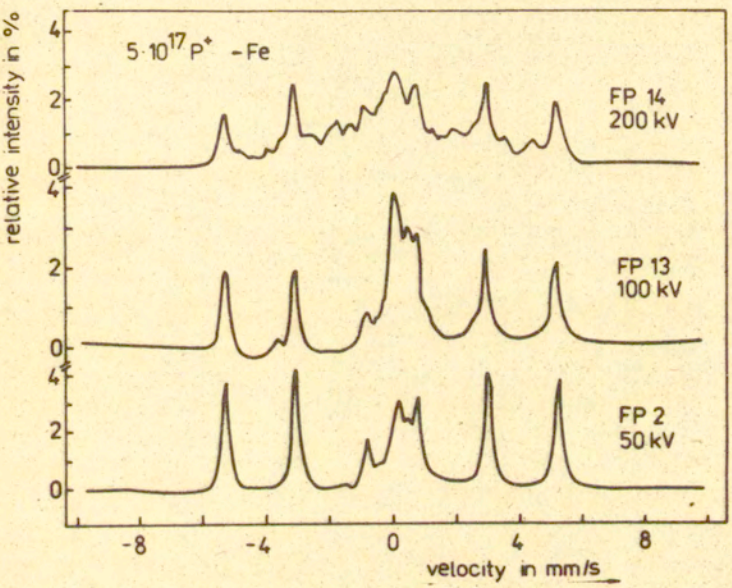
Rys. 2 Mossbauer spectra of nitrogen implanted iron /1,2x10^{18}N/cm^2, 50 kV/



Rys. 3. Distribution of phosphorus /full lines/ and nitrogen /dashed lines/ in iron after implantation at various voltages, calculated according to /2/ implantation dose $1x10^{17}cm^{-2}$/



Rys. 4. Mossbauer spectra of phosphorus implanted iron /6x10^{16} to 6x10^{17} P/cm^2, 50 kV/



Rys. 5. Mossbauer spectra of phosphorus implanted iron /5x10^{17} P/cm^2, 50, 100, 200 kV/