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The Influence of the Defect Structure on the Nitriding of Fe by PIII

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Plasma ion immersion implantation is a promising technique for nitriding. A case study of the characterization of the plasma ion immersion implantation nitriding of iron alloys is the plasma ion immersion implantation nitriding of pure Fe. A set of Fe samples of 99.98% purity and with different defect structure was plasma ion immersion implantation nitrided at different temperatures. Depth profiling of the samples was achieved using positron annihilation spectroscopy with a slow positron beam and nanoindentation. A correspondence was found between the line shape parameter S and the hardness of the plasma ion immersion implantation treated samples.

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1. Sample preparation

Discs of 15 mm diameter and 2 mm thickness were prepared from an iron rod of 3N8 purity. The specimens were ground and polished and annealed in vacuum at 850°C for 1 h followed by a cooling (1°C/min) down to room temperature to remove defects that were introduced during specimen machining. The specimens were divided into three groups denoted A, P, and E. Samples of group A were kept in the annealed state, P and E specimens were surface ground and polished to a 1 μm diamond mirror finish, and finally after the polish the surface of the E

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specimens was electrochemically etched. For the electrochemical etching a solution of 90 ml of glacial acetic acid with 10 ml perchloric acid was used as electrolyte at 40 V for 1 min, resulting in a thickness of the removed surface layer of approximately 1 μm. Plasma ion immersion implantation (PIII) was performed by the MARK-1 device [1] using a hot wall system at 300, 400, and 500°C for 3 h. The pulses were set at 100 Hz and 100 ms at 30 kV. The plasma was generated at a nitrogen pressure of 1×10^{-2} mbar and 300 W rf-power resulting in an average dose of 1.8×10^{18} at/cm^2 for all specimens.

2. DBAR measurements

The Doppler broadening of the annihilation radiation (DBAR) measurement were performed using the Ghent Slow positron facility which is fully described in [2]. Depth profiling was achieved by varying the implantation energy of the slow positrons from 0.1 to 30 keV corresponding to mean implantation depths up to 1 μm. The results are presented in Fig. 1 using the S line shape parameter.

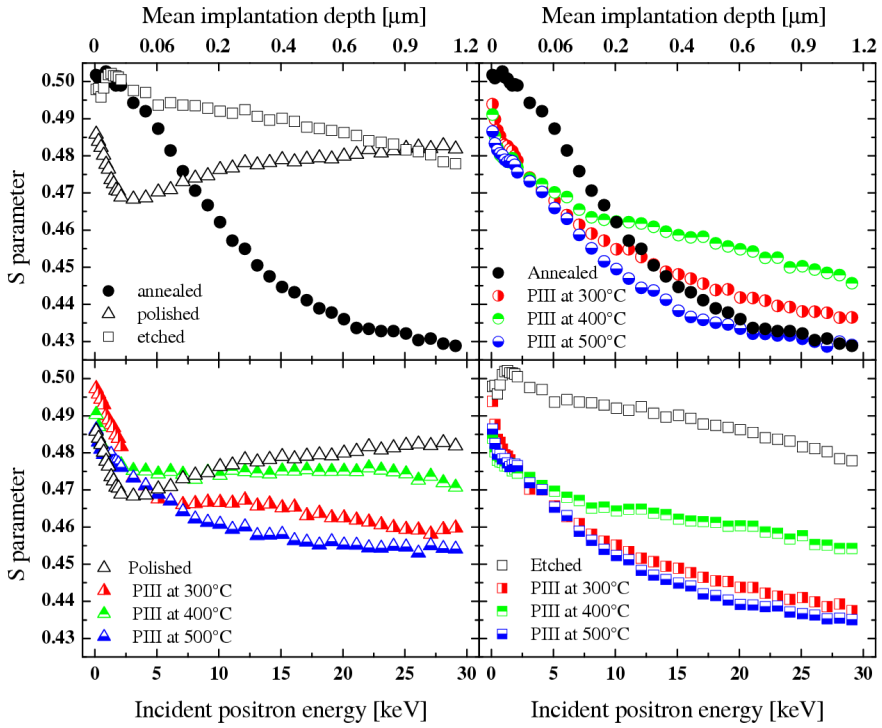

Fig. 1. DBAR S parameter depth profile of iron samples prior and after PIII nitriding at different temperatures.

The virgin annealed sample shows a surface S parameter of 0.502 which evolves down to a value of 0.430 corresponding to the defect free state. This is

confirmed by positron annihilation lifetime measurements. The positron lifetime of the virgin annealed sample is 105 ps, this value is in good agreement with the literature value of 106 ps for defect free Fe [3]. The polished sample shows a surface layer (probably oxide) indicated by a decreasing S parameter from the surface up to an incident energy of 2.5 keV corresponding to a mean implantation depth of 20 nm. Deeper in the sample the S parameter increases from a value of 0.468 to values higher than 0.480. This indicates the presence of open volume defects deeper than 1 μm due to the polishing and a change of either the defect type or the defect concentration in function of depth. The etched sample also shows a surface layer of several nm. The high S value of 0.480 at 1 μm for the etched sample also indicates that the etching did not fully remove the defectuous zone introduced by the polish.

For all the PIII treated samples a top layer is visible indicated by a decreasing S from the surface up to a mean implantation depth of 20 nm. This value corresponds to the top of the vacancy profile calculated by transport of ions in matter (TRIM) [4] for nitrogen ions implanted in iron with an incident energy of 30 keV [5]. The treatment temperatures do not seem to remove this defect structure. The signature of the subsurface layer introduced by the polishing vanishes for treatment temperatures higher than 300°C. The S parameter at 1 μm for all the samples is presented in Fig. 2a. For each implantation temperature the polished sample has the highest S value followed by the etched sample. For the different treatment temperatures the S parameters are the highest for the PIII at 400°C and the lowest for the PIII at 500°C.

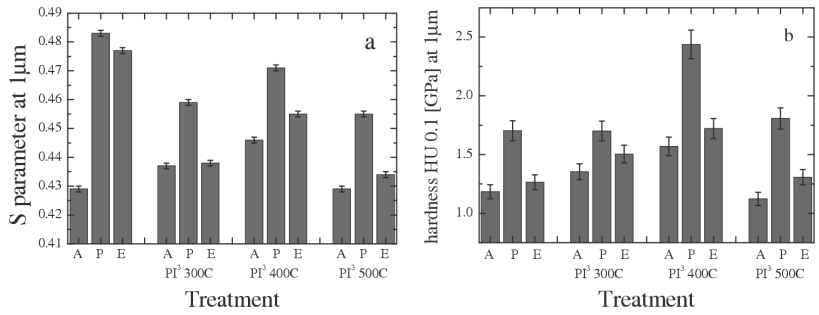

Fig. 2. (a) S parameter at 1 μm; (b) hardness at 1 μm.

3. Nanoindentation analysis

Depth profile nanoindentation measurements were performed using a FISCHER HV 100 XYProg. The results of the nanoindentation measurements are summarized by presenting the hardness at 1 μm in Fig. 2b. The samples PIII treated at 300°C are significantly harder than the virgin samples for the annealed and the etched sample. The implantations at 400°C result in the overall hardest

layers. It must also be noticed that only these samples show a pronounced subsurface (100 nm $\longleftrightarrow$ 250 nm) region with a hardness of 3 GPa for the annealed and etched samples and a value of 6 GPa for the polished sample. The polished sample PIII treated at 400°C has the highest hardness of all the investigated samples. The hardness depth profiles for the implantations at 500°C are almost identical to those of the virgin samples.

4. Discussions

The comparison in Fig. 2 between the line shape parameter S at 1 μm and the hardness at the same depth shows that the overall evolution for the PIII treated samples coincides. This is however not the case for the virgin samples. While the remaining defect structure after the etching is clearly visible for the DBAR analysis, it has only limited influence on the hardness of the sample. The hardness of a material depends on both the presence of defects such as dislocations which hinder dislocation movement and the chemical bonds. The nitrogen content and Fe–N phases of an identical set of samples was investigated by Jirásková et al. [6]. The polished and etched samples showed an increase in relative representation of Fe–N phases with high nitrogen content (γ-Fe_4N, ε-$Fe_{3-x}N$, and ε-Fe_2N). It can thus be concluded that the presence of these nitrides results in the hardening of the material and the increase in the S parameter. The formation of interfaces between the nitrides and the α-Fe matrix with additional transformation dislocations increases the hardness and the S parameter. The S parameter can however also be increased by the decrease in the average electron density in the nitrides [7].

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