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COMPOSITIONAL AND MICROSTRUCTURAL ANALYSES OF Fe-Pd NANOSTRUCTURED THIN FILMS

ELEMENTNA IN MIKROSTRUKTURNA ANALIZA NANOSTRUKTURNIH TANKIH PLASTI Fe-Pd

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Fe-Pd thin films with various compositions and thicknesses were produced with electrodeposition using the constant potentials from –1.0 to –1.3 V. The FEGSEM and AFM analyses revealed a smooth, nanostructured surface morphology of the films, with more granular features appearing at more negative potentials. The high-resolution FEGSEM images of the film cross-sections and complementary calculations using the data from the EDS thin-film analyses were used to determine the film thicknesses, showing that ultrathin films 50 nm to 120 nm were obtained. The chemical compositions of the films were measured with a quantitative, EDS electron-probe microanalysis using two independent approaches: (i) a low-voltage analysis (LVEDS) and (ii) a variable-voltage analysis with a dedicated thin-film-analysis (TFA) method. Both approaches were properly modified and optimized on the basis of the Monte Carlo simulation data. The results showed that the composition of the Fe-Pd films was close to the preferred equiatomic $Fe_{50}Pd_{50}$ stoichiometry (which is important for achieving good magnetic properties) and was obtained at –1.3 V and –1.2 V. At the more positive potentials, the Fe-Pd films became Pd rich. The best agreement between the LVEDS and TFA quantitative results was achieved for the Fe-Pd films that were thicker than 80 nm, and a slight discrepancy within the ±10 % relative between the LVEDS and TFA values was observed for the films thinner than 70 nm. The faster LVEDS approach is suitable for routine analyses of numerous Fe-Pd samples, to obtain the information about a film composition in a short time. The more demanding TFA approach was found to be very appropriate for accurate compositional analyses of the Fe-Pd ultrathin films and for determining the film thickness.

Keywords: Fe-Pd films, electron-probe microanalysis, FEGSEM, EDS, AFM

Tanke plasti na osnovi zlitine Fe-Pd z različno sestavo in debelino smo pripravili z metodo elektronanosa pri konstantnih potencialih od –1,0 V do –1,3 V. S FEGSEM- in AFM-preiskavami morfologije smo ugotovili, da je površina plasti gladka in sestavljena iz nanodelcev, katerih velikost narašča z uporabo bolj negativnih potencialov. Debelino plasti smo določili iz visokoločljivostnih FEGSEM-posnetkov prerezov plasti in dodatno z izračuni na osnovi podatkov iz EDS-analiz. Sintetizirane plasti Fe-Pd so imele debelino med 50 nm in 120 nm. Kemijsko sestavo takšnih ultratankih plasti smo določili s kvantitativno elektronsko mikroanalizo z EDS z uporabo dveh neodvisnih metod: (i) z analizo pri nizki pospeševalni napetosti (LVEDS) in (ii) analizo pri spremenljivih napetostih s posebnim postopkom za analizo tankih plasti (TFA). Analitski metodi smo priredili in optimirali na osnovi izračunov, narejenih s simulacijo Monte Carlo. Zaželena stehiometrija $Fe_{50}Pd_{50}$, ki je pomembna s stališča doseganja dobrih magnetnih lastnosti, je bila dobljena pri potencialih –1,3 V in –1,2 V, medtem ko so bile plasti, narejene pri bolj pozitivnih napetostih, bogate s Pd. Rezultati kvantitativnih analiz LVEDS in TFA so bili konsistentni in so se odlično ujemali za plasti Fe-Pd, ki so bile debelejše od 80 nm. Pri plasteh, tanjših od 70 nm, smo ugotovili majhen odmik rezultatov LVEDS v primerjavi s TFA, in sicer v okviru relativne razlike ±10 %. Hitrejša LVEDS-metoda je primerna za rutinske analize in določanje sestave večjega števila Fe-Pd-vzorcev. Zahtevnejša metoda TFA je bolj natančna in večstranska, saj poleg analize sestave ultratankih Fe-Pd-plasti omogoča tudi določanje debeline le-teh.

Ključne besede: tanke plasti Fe-Pd, elektronska mikroanaliza, FEGSEM, EDS, AFM

1 INTRODUCTION

Thin films made from Fe-Pd alloys with a stoichiometry close to the equiatomic Fe/Pd ratio and an ordered $L1_0$ phase have attracted a lot of attention because of their large magnetocrystalline anisotropy (1.8 MJ/m^3) and the consequent good hard-magnetic properties, which can be retained even at the nanoscale.[1] Such properties make these materials suitable for high-density, perpendicular, magneto-recording media or for the nanodevices in nanoelectromechanical systems (NEMS).[1–3] Fe-Pd thin films can be prepared by electroplating, which is a cost-effective and efficient method, with a possibility of tailoring a film composition and morphology via simple experimental adjustments. An electrochemical synthesis of Fe-Pd thin films basically depends on the preparation of a stable electrolyte and, recently, successful Fe and Pd co-depositions were performed in a citrate-based bath.[4] Different kinds of thin-film applications would require thin films with well-defined properties resulting from an electrochemical processing. The initial Fe- and Pd-ion concentrations, the applied potential, the deposition time, etc., are the parameters that influence a film chemical composition, thickness, surface roughness and microstructure, all of which have an impact on the final properties.

In order to investigate the influence of the parameters of an electrodeposition process on the composition and microstructure of Fe-Pd thin films and to define the composition-property relations, it is important to perform a reliable microstructural and compositional characterization of the as-deposited films.

For this purpose a high-resolution field-emission-gun scanning electron microscope (FEGSEM) combined

with an electron-probe microanalysis (EPMA) using energy-dispersive X-ray spectroscopy (EDS) can be used as an appropriate characterization tool. However, since the thickness of Fe-Pd films is in the submicrometer/nanometer range, the analytical procedure for the quantitative EDS measurements is not straightforward and it requires special attention in order to achieve precise and accurate analytical results.[5–7] For this reason, in this work, we propose two advanced, independent and optimized EDS procedures that were applied to determine the chemical composition of thin Fe-Pd films with high confidence. The high-resolution FEGSEM imaging and atomic-force microscopy (AFM) were employed to study the quality of the film surfaces, the surface morphology and the film thickness.

2 EXPERIMENTAL WORK

The Fe-Pd thin films were produced with an electrodeposition from an electrolyte based on palladium chloride $PdCl_2$ 2 mM, iron chloride $FeCl_2$ 18 mM, ammonium citrate (NH_4)2C6H6O7 0.2 mM and NH3(aq) 0.5 M with pH = 9.[4,8] The potentiostatic co-deposition of Fe and Pd was performed at the potentials of –1.00, –1.10, –1.15, –1.20 and –1.30 V measured vs. an Ag/AgCl electrode, for 300 s, onto a SiO_2-glass substrate that was plasma-sputtered with Cr 40 nm and Au 100 nm metallic layers.

The characterization of the Fe-Pd samples was carried out in a FEGSEM JEOL JSM-7600F equipped with a high-efficiency, silicon drift EDS detector (SDD) X-Max 20 and an INCA microanalysis suite from Oxford Instruments. FEGSEM micrographs were recorded using secondary electrons (SE) or backscattered electrons in the compositional contrast mode (BSE-COMPO). Complementary AFM images were recorded with a Veeco diDimension 3100 scanning probe microscope in the tapping mode. To avoid the charging in the SEM the film cross-sections were coated with a 3 nm-thick amorphous carbon conductive layer in a Gatan PECS 682. After considering the complex, stratified arrangement of the samples, i.e., the Fe-Pd/Au/Cr metallic layers on the SiO_2 substrate, Monte Carlo (MC) simulations were performed in order to decide on the optimum experimental conditions for the quantitative EDS analyses.[9,10] Consequently, two independent SEM/EDS experimental set-ups were applied:

i. a low-voltage EDS analysis (LVEDS) of the low-energy Fe-Lα (0.704 keV) and Pd-Lα (2.838 keV) spectral lines at the SEM accelerating voltage of 6.5 kV,
ii. variable-voltage analyses at (13, 15, 17 and 19) kV of all the elements present in the Fe-Pd films and in the substrate, by measuring the spectral lines of Fe-Kα (6.403 keV), Pd-Lα, Au-Mα (2.123 keV), Cr-Kα (5.414 keV), Si-Kα (1.740 keV) and O-Kα (0.523 keV), followed by an off-line EDS-data processing with a dedicated thin-film analysis method (TFA).[11]

To improve the accuracy of the quantitative analysis, the EDS-SDD detector response was properly calibrated at each applied accelerating voltage using Co and Si as standard reference materials. The EDS spectra were quantified using the XPP-$\Phi(\rho z)$ matrix-correction procedure.[11]

3 RESULTS AND DISCUSSION

The SEM micrographs of the surfaces of the two representative Fe-Pd films deposited at –1.0 V and –1.3 V are shown in **Figure 1**. We found that at a higher absolute value of the applied voltage (≥1.2 V) the surfaces of the films become more granular, with bubble-like features (**Figure 1b**), which is due to an increased cathodic hydrogen evolution, whereas at lower absolute voltages (≤1.15 V) smoother nanostructured films were obtained (**Figure 1a**). Characteristic surface-profile parameters were determined from the corresponding AFM images, acquired from the 2 μm × 2 μm sized regions on the samples, as presented in **Figure 2**. The three-dimensional image analyses revealed that the maximum profile height difference (z) was 40 nm at –1.0 V and 105 nm at –1.3 V, with the respective average-roughness (R_a) values of 2 nm and 10 nm. These data were taken into account in order to apply a suitable EDS measurement strategy that effectively diminishes

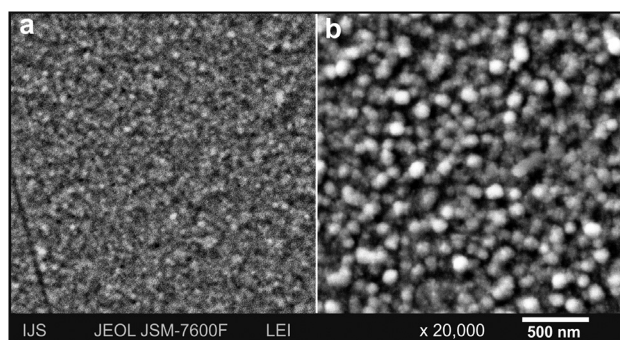

Figure 1: FEGSEM SE micrographs of the surface morphology of Fe-Pd films: a) deposited at –1.0 V, b) deposited at –1.3 V

Slika 1: FEGSEM SE-posnetka morfologije površine plasti Fe-Pd: a) plast, nanesena pri –1,0 V, b) plast, nanesena pri –1,3 V

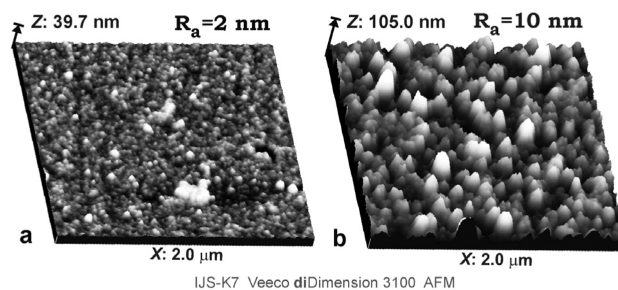

Figure 2: AFM images of Fe-Pd films deposited at: a) –1.0 V and b) at –1.3 V

Slika 2: AFM-posnetka plasti Fe-Pd, nanesenih pri: a) –1,0 V in b) –1,3 V

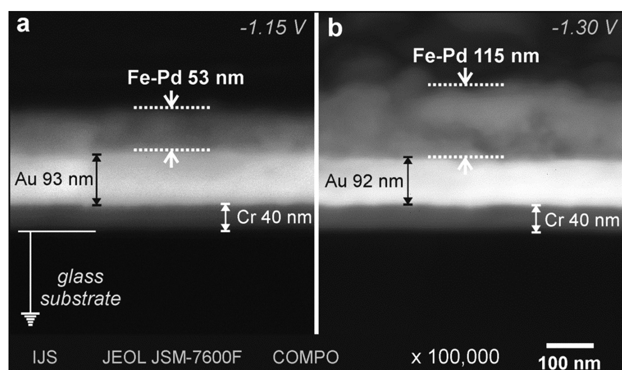

Figure 3: FEGSEM BSE-COMPO micrograph of the cross-sections of Fe-Pd films: a) deposited at –1.15 V, b) deposited at –1.3 V

Slika 3: FEGSEM BSE-COMPO-posnetek prečnega prereza plasti Fe-Pd: a) plast, nanesena pri –1,15 V, b) plast, nanesena pri –1,3 V

the influence of the roughness on the spectral-data acquisition.

The high-resolution compositional contrast micrographs of the cross-section samples of the Fe-Pd films deposited at –1.15 V and –1.3 V are shown in **Figure 3**. This imaging mode emphasizes the grey-level differences between the materials/elements according to the differences in their (average) atomic numbers. So, the micrographs clearly revealed the layered structure of the samples with a Fe-Pd film on the top of the $Au/Cr/SiO_2$ substrate. The thickness of individual metallic layers was measured directly from the images, taking six random positions on the samples with the average values given on the images (**Figure 3a, b**). The results obtained for all the analysed samples showed that the Fe-Pd films have the thicknesses in the range from 50 nm to 120 nm.

On the basis of the MC calculations the applied voltage 6.5 kV for the LVEDS set-up was found to be an appropriate compromise choice that ensures a sufficiently small size of the X-ray analytical volume and a large enough overvoltage ratio to maintain a level of ≥2 for the highest X-ray energy analysed, i.e., the L_3-edge excitation energy of the Pd-Lα radiation. Consequently, using the LVEDS the analytical procedure gets closer to the conventional bulk-sample EPMA situation, as illustrated in **Figure 4**, showing the MC results for the 85-nm-thick Fe-Pd film. The maximum X-ray generation depth at 6.5 kV (X-ray range) is ≈110 nm, suggesting that some Au-Mα X-rays may still be generated from the Au-layer beneath the Fe-Pd film on the top, especially in the case of the films thinner than 100 nm. The $\Phi(\rho z)$ depth-distribution curves given in **Figure 4** also show a minor Au-Mα contribution, together with the principal contributions of the Pd-Lα and Fe-Lα lines. The X-ray intensity calculations revealed that a high absorption of the Fe-Lα radiation occurs with ≈60 % of the generated X-rays being absorbed in the Fe-Pd matrix, whereas this effect is negligible for the Pd-Lα line. Even so, an acceptable accuracy of the quantitative LVEDS can be achieved, since it is expected that the XPP matrix correction is capable of compensating for the strong absorption effects, like those present here for the Fe-Lα line.

The comparison of the characteristic EDS spectra acquired from the Fe-Pd film 85 nm using the LVEDS and TFA approaches is shown in **Figure 5**. As predicted from the MC calculations, the spectrum 6.5 kV has two main peaks, Fe-Lα and Pd-Lα, and a minor Au-Mα peak. The appearance of the small O-Kα peak is (most likely) due to a partial film-surface oxidation upon the film preparation. The Au-M and O-K contributions were then neglected in the quantification and calculation of the Fe/Pd stoichiometry. The spectrum 19 kV (and also the spectra at (13, 15 and 17) kV) shows the peaks of all the elements from the film and the substrate: Fe, Pd, Au,

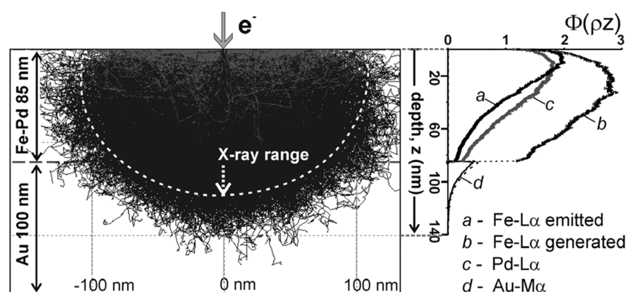

Figure 4: Results of the Monte Carlo simulation performed for the 85-nm-thick Fe-Pd film sample at the beam energy 6.5 keV. The image shows the size of the electron interaction volume in the *x–z* projection, the estimated size of the X-ray generation range and the $\Phi(\rho z)$ depth-distribution intensity curves for the Fe-Lα, Pd-Lα and Au-Mα spectral lines.

Slika 4: Rezultati simulacije Monte Carlo za vzorec plasti Fe-Pd debeline 85 nm pri energiji elektronov 6,5 keV. Slika prikazuje velikost interakcijskega volumna elektronov v projekciji *x–z*, oceno velikosti področja nastanka rentgenskih žarkov in $\Phi(\rho z)$-krivulje globinske porazdelitve intenzitet za spektralne črte Fe-Lα, Pd-Lα in Au-Mα.

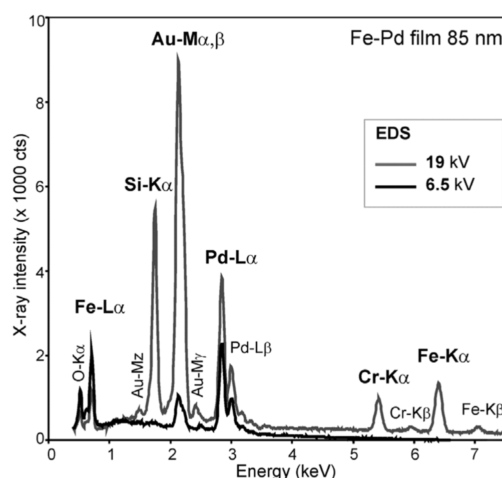

Figure 5: Comparison of the EDS spectra at 6.5 kV and 19 kV, obtained from the Fe-Pd film 85 nm, with marked analytical spectral lines used for the LVEDS and/or TFA methods

Slika 5: Primerjava EDS-spektrov pri 6,5 kV in 19 kV, ki so bili pridobljeni iz 85 nm tanke plasti Fe-Pd, z označenimi analitskimi spektralnimi črtami, ki so bile uporabljene za metodi LVEDS in/ali TFA

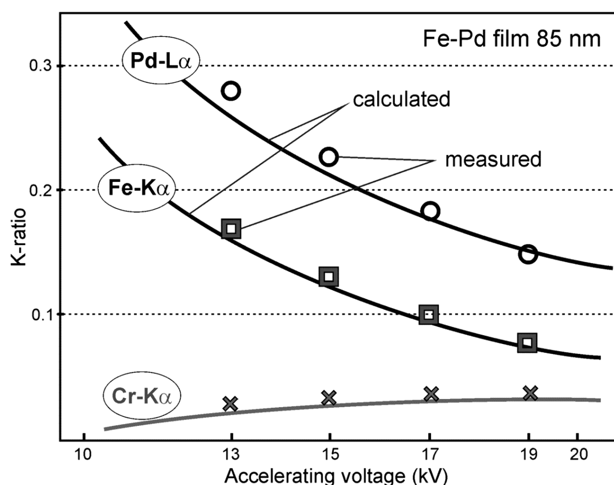

Figure 6: Calculated and measured Fe, Pd and Cr *k*-ratio values versus the accelerating voltage, obtained using EDS-TFA analyses

Slika 6: Izračunane in izmerjene vrednosti *k*-razmerij za Fe, Pd in Cr v odvisnosti od pospeševalne napetosti, dobljene z analizami EDS-TFA

Cr and Si. In the case of the TFA, we found, with the MC calculations, that the O-Kα radiation from the SiO_2 substrate is fully absorbed in the upper layers at all the applied voltages. The EDS-TFA spectra were subsequently processed to obtain the dependence of the measured and calculated k-ratios versus the voltage, as shown in **Figure 6** for Fe, Pd and Cr. The excellent fit obtained for the measured and calculated values verifies the correctness of the TFA experimental set-up and ensures that a reliable quantitative compositional analysis of the Fe-Pd films can be achieved. Consequently, the true X-ray depth distributions were computed for the stratified Fe-Pd/Au/Cr/SiO_2 specimens, which then allowed us to calculate the Fe-Pd film thicknesses with high confidence as well.

The reliability of the TFA was first assessed with a comparison of the film-thickness results for the intermediate Au and Cr layers that were obtained from the SEM images and from the TFA calculations, as shown in **Figure 7**. Taking into account that the inherent precision of the plasma-sputtering device is ≤±15 % relative, the experimentally determined values for the Au- and Cr-layer thicknesses were fully consistent with their declared/nominal values, which was an additional proof of the accuracy of the TFA method. The results of the thickness determination for the Fe-Pd films are given in **Figure 8**. The comparison of the SEM and TFA values showed a very good agreement between the two datasets, i.e., similar thickness values were independently determined with both methods. Thus, under the applied electrodeposition conditions, the ultrathin Fe-Pd films with the thicknesses between ≈50 nm and 120 nm were produced.

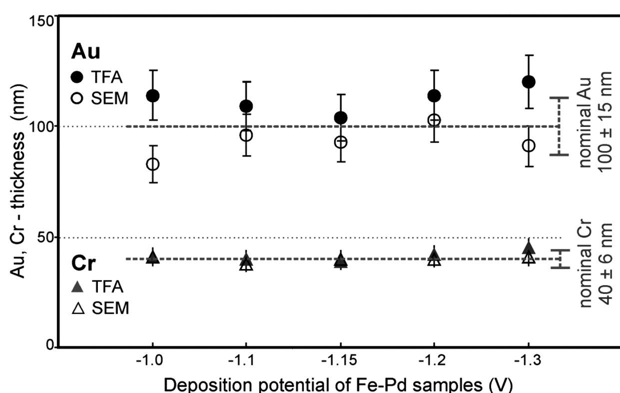

Figure 7: Measured thickness values for the Au and Cr intermediate layers, determined directly from the SEM images and calculated from the TFA data

Slika 7: Izmerjene vrednosti debelin vmesnih plasti Au in Cr, določene neposredno iz SEM-posnetkov in izračunane na osnovi podatkov iz analiz TFA

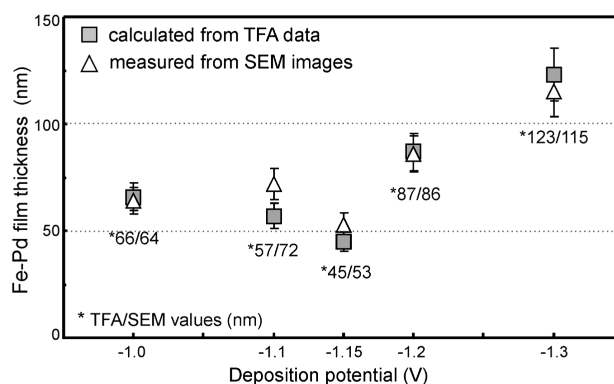

Figure 8: Thickness of the Fe-Pd films versus the applied deposition potential, determined from the SEM images and from the TFA data

Slika 8: Debelina plasti Fe-Pd v odvisnosti od napetosti nanašanja, določene iz SEM-posnetkov in na osnovi podatkov iz analiz TFA

A summary of the results of the EDS quantitative elemental analyses performed by the LVEDS and TFA is given in **Figure 9**. The composition of the Fe-Pd films close or equal to the preferred equiatomic $Fe_{50}Pd_{50}$

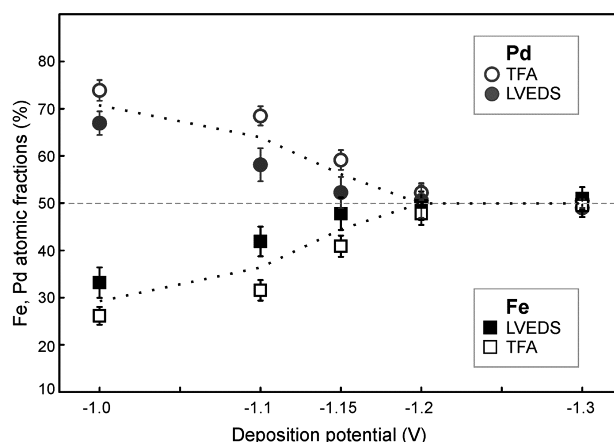

Figure 9: Fe and Pd elemental atomic fractions (%) versus the deposition potential of the analysed Fe-Pd films, as determined from the quantitative LVEDS and TFA methods

Slika 9: Atomski deleži (%) za Fe in Pd v odvisnosti od napetosti nanašanja analiziranih vzorcev plasti Fe-Pd, določeni iz kvantitativne analize z metodami LVEDS in TFA

stoichiometry was obtained at higher absolute deposition potentials, i.e., at –1.2 V and –1.3 V. At lower absolute potentials (i.e., ≥–1.15 V) the Fe-Pd films are Pd rich due to the more positive reduction potentials of the Pd-complex in comparison with the Fe-complex. It is evident that the best agreement between the LVEDS and TFA quantitative data is achieved for the Fe-Pd films that are thicker than ≈80 nm, whereas for the films below 70 nm, a certain discrepancy is present. This discrepancy, in the case of the very thin Fe-Pd samples, is due to the additional X-ray excitations originating from the substrate (Au), even at 6.5 kV, where the bulk-sample analysis approximation becomes less correct. Namely, both the Pd-Lα radiation excited from the Fe-Pd layer and a certain quantity of the primary-beam electrons can produce the Au-Mα X-rays, either by the secondary fluorescence or by the primary ionization process. Furthermore, the photons of the Au-Mα partially contribute to the extra Fe-Lα excitations by the secondary fluorescence as well. Since these effects are complicated and difficult to calculate, they are neglected in the LVEDS approach and, therefore, the seemingly higher Fe concentrations in the very thin Fe-Pd samples were obtained with the LVEDS analysis, as compared to the TFA. Subsequently, a correct analysis of the Fe-Pd films can be performed using the procedures designed for the bulk-like samples (LVEDS), when no extra radiations are emitted due to the fluorescence of the substrate excited by the film. Even so, these discrepancies between the LVEDS and TFA quantitative results are relatively small and within ±10 % relative.

4 CONCLUSIONS

The composition and microstructure of the electrodeposited Fe-Pd thin films were studied by the FEGSEM, EDS and AFM. The Fe-Pd films had a nanostructured surface morphology with an increased roughness at higher absolute values of the deposition potential. The film thickness varied from 50 nm to 120 nm. In order to analyse the chemical composition of such ultrathin Fe-Pd layers on the Au/Cr/SiO_2 substrate, two specially designed quantitative EDS methods were applied, i.e., the LVEDS and TFA. The LVEDS approach gave good accuracy for the Fe-Pd films thicker than 80 nm and reasonable results for the thinner films (<70 nm), being within the ±10 % relative difference in comparison with the TFA quantitative results. Since the LVEDS approach is quicker, it is suitable and acceptable for a routine control of the Fe/Pd stoichiometry for a large number of the samples produced in laboratory experiments every day. The optimized, dedicated TFA approach was found to be a very appropriate and accurate method for a quantitative compositional analysis of the Fe-Pd thin films and for the film-thickness determinations as well. Since reliable and accurate quantitative results can be achieved for any film thickness, we recommend using this, admittedly more demanding, TFA approach, particularly for analysing ultrathin Fe-Pd films.

Acknowledgements

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