Quantitative EPMA of electrodeposited thin Co-Pt films – assessment of reliability and accuracy

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Quantitative electron-probe microanalysis (EPMA) with energy-dispersive (EDS) and wavelength-dispersive (WDS) X-ray spectroscopy was applied for compositional analyses of ferromagnetic Co-Pt thin films that were produced by electrodeposition on an Au/Cr/SiO_2 substrate [1]. The study deals with conventional "bulk" microanalysis, as this is the most widespread and accessible EPMA application. Quantitative analyses were performed with (i) the common standardless EDS method and (ii) EDS and WDS analyses using pure Co and Pt metallic standards. The Co-Pt films with thicknesses 140, 200, 460, 740 and 1040 nm were analyzed at 20- and 7-keV beam energies using various experimental set-ups with different combinations of analytical spectral lines (Co-K,L and Pt-L,M) and quantitative matrix-correction programs $\Phi(\rho z)$ and ZAF [2,3]. The results were critically reviewed in order to assess the reliability and accuracy of the quantitative microanalyses.

The Monte Carlo simulations showed that at 20 keV the Co-Pt films thicker than 600 nm act as bulk samples, whereas thinner films, down to 120-nm thickness, can be analyzed at 7 keV using the low-energy Co-Lα and Pt-Mα spectral lines. A detailed comparison of the analytical results obtained for a 1040-nm-thick Co-Pt film is given in Fig. 1a. The graph clearly shows that the WDS results are fully consistent and practically independent of the analytical set-up. All the WDS data points fall within $\pm 1\sigma$ of the "average WDS" line, which was calculated and added as a reference for the evaluation. In contrast, the EDS results display significant scatter with large differences between the set-ups as well as between the two applied EDS systems. Furthermore, the results revealed that the quantification of the same EDS spectrum can give very different results, depending on the choice of analytical spectral lines and the matrix correction. The best EDS results, comparable to the WDS, were obtained at 20 keV by analyzing the Co-Kα and Pt-Lα lines; however, it works properly only on thicker "bulk-like" Co-Pt films. The quantification of the Pt-Mα line instead of the Pt-Lα gave increased scatter with big differences between the applied EDS systems.

The results of the 7-keV EDS analyses deviate the most, showing a significant influence of the type of matrix correction on the results. An additional EDS analysis with standards gave similar or only slightly better results as compared to the commonly used standardless method. At 7-keV the best EDS analysis still gave an overestimated Co concentration and an underestimated Pt concentration, determined to have an error of ≈ 6 %, relative to the average WDS reference values. The values for the Co/Pt atomic ratios calculated from the WDS and the closest EDS analyses are presented in Fig. 1b. The EDS Co/Pt ratios are systematically overestimated, with a discrepancy from 10 % to 70 % relative to the WDS. Consequently, in routine SEM/EDS work a microanalysis at a low beam energy (7 keV) has to be treated with great caution and can only be used for a rough estimation of the Co-Pt thin film's composition, taking into account the significant errors that can occur.

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The presented results revealed that a quantitative EDS analysis of Co-Pt thin-films, although seemingly a simple analytical task, is not that straightforward and must be critically reviewed to evaluate the reliability and accuracy of the obtained results. The inconsistency of the EDS analyses can be attributed to the shortcomings within so-called "black-box" EDS standardless-analysis software packages. The intrinsically low analytical sensitivity of the EDS method and possible peak overlaps also have to be considered as the limiting factors for the accuracy.

In contrast, by using the WDS we were able to determine the composition of the Co-Pt thin films with a superior analytical sensitivity, high precision and an ultimate accuracy of < 1 % relative. An optimized WDS "bulk" microanalysis performed at low beam energies and by measuring the low-energy Pt-Mα and Co-Lα spectral lines was found to be the most accurate and fully reliable for quantitative compositional analyses of Co-Pt thin films with a thickness down to ≈ 100 nm. An accurate quantitative microanalysis has an important role in the study of the influence of the electrodeposition process parameters on the composition and properties of Co-Pt thin films.

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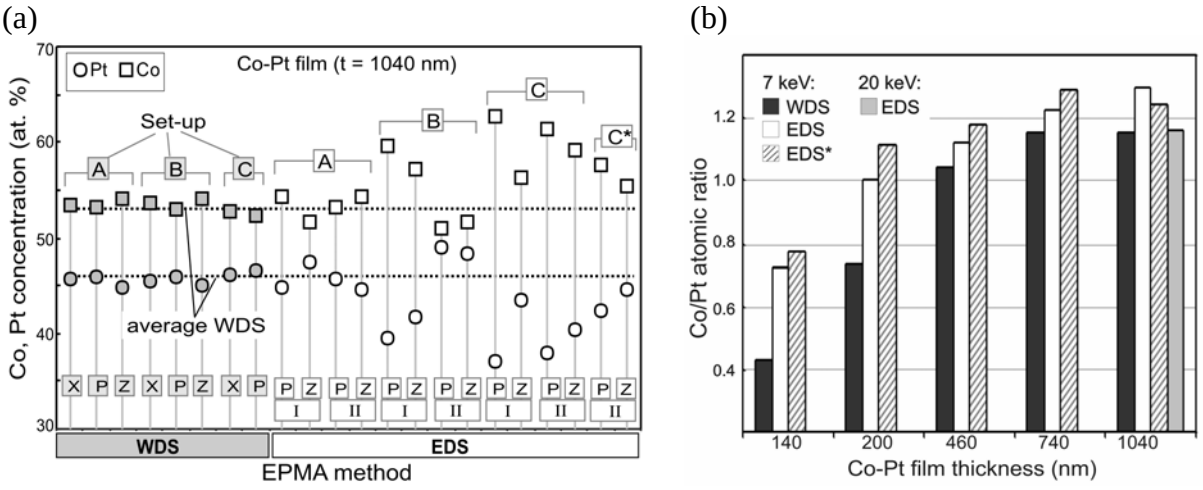

Figure 1. (a) The overall results of EDS and WDS quantitative analyses of the 1040-nm-thick Co-Pt film, given for different analytical set-ups: A – 20 keV/Co-Kα/Pt-Lα, B – 20 keV/Co-Kα/Pt-Mα and C – 7 keV/Co-Lα/Pt-Mα; for three applied matrix-correction methods: X – Φ(ρz) *XPHI* [2], P – Φ(ρz) *PROZA* [3] and Z – conventional ZAF method; and for two EDS systems: I – Oxford Link ISIS 300 and II – Tracor Series II X-ray Microanalysis System. * denotes EDS analysis with standards. (b) Comparison of values for the Co/Pt atomic ratios calculated from the WDS and EDS analyses.

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