

## Reply to ‘Comment on “Calibration of nitrogen content for GDOES depth profiling of complex nitride coatings”’ by V. Hoffmann, *J. Anal. At. Spectrom.*, 2008, 23, DOI: 10.1039/b713743p

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In the last few years, there has been an increasing interest within the material science community in the use of GDOES to analyze the compositional depth profiles of thin films and coatings for a wide range of applications (*i.e.*, hard protection for mechanical parts and tools, optical coatings for lenses and architecture panels, barrier contacts for microelectronics, or in biomedical prosthesis). Most of these films consist of combinations of metal and/or metal compounds (oxides, nitrides, carbides, *etc.*) in order to achieve the desired properties. Therefore, one of the main impediments for a more extensive use of GDOES in the analysis of such samples lies in the lack of good calibration samples for quantitative analysis of light elements such as oxygen or nitrogen. Regarding nitrogen calibration, it is worth mentioning the Round Robin exercise performed by Hodoroaba *et al.*<sup>1</sup> for the analysis of nitride layers with GDOES and the more recent work of Baunack *et al.*<sup>2</sup> comparing results of GDOES and Auger electron spectrometry (AES). In this context, the article by Escobar Galindo *et al.*<sup>3</sup> was submitted as a Technical Note mainly because the work was aimed at presenting a practical tool within this very important topic.

The novelty of the work rests on the in-house preparation and characterisation of chromium nitride layers to be used as calibration samples, in combination with an absolute technique as RBS to assess their chemical composition. The purpose of the article was to present such a method and make it available to GDOES users that might find it useful and, with the proper means, “relatively easy” to implement in order to improve their calibration lines. It was in particular addressed to research groups and technological centres using thin film deposition techniques (PVD, CVD; *etc.*). These groups could prepare the nitride coatings and use the proposed calibration as a fast feedback test to assess the conditions of their deposition processes.

By no means was the aim of the article to generate “the false impression that “the relatively easy way of calibrating GDOES for nitrogen analysis” using CrN<sub>x</sub> layers solves the problem of accuracy at the quantification of nitrogen in GDOES” as suggested by Hoffmann in his Comment.<sup>4</sup> It should be also clear that there was no intention to use these layers as Certified Reference Materials (at least at this stage). In fact, the CrN<sub>x</sub> coatings are specifically referred to in the text as “calibration samples” and never as CRM’s. As indicated by Hoffmann, before such samples can replace CRM’s a direct method for the

determination of the layer density must be provided. However, as stated before, that was not the purpose of the work.

The proposed calibration strategy might not be the most precise procedure and we agree with Hoffmann<sup>4</sup> that, surely, more fundamental studies should be performed (similar to those performed by Baunack *et al.*<sup>2</sup>). Of special interest would be the determination of the matrix independence of the calibration proposed by measuring materials with different emission yield. In fact the concept of constant emission yield approach has been extensively discussed in a recent review by Bengtson and Nelis,<sup>5</sup> although, we believe the depth of that discussion goes far beyond the aim of this practical Technical Note. Certainly, the validation of the proposed calibration with CRM containing nitrogen as the JK41 (6.9 wt%) and JK 49 (1.89 wt%) standards from Jernkontoret would also be of interest.<sup>6</sup> We are in the process of obtaining such samples and we expect that, before long, we could report on the comparison with our CrN<sub>x</sub> layers.

The main concerns expressed by Hoffmann<sup>4</sup> on the accuracy of the calibration are related to the preparation of the CrN<sub>x</sub> and TiN layers. In our work, the thickness of the CrN<sub>x</sub> sputter deposited layers was measured using a stylus profilometer (Dektak 3030) and corroborated after close Scanning Electron Microscopy examination in cross sectional mode in order to obtain accuracies in the nanometre range.<sup>7</sup> The erosion rates of the layers were determined in the same way as done for all the calibration samples, by measuring 5 replicas of the crater depth with a profilometer obtaining a relative error of less than 10%. The incorporation of argon ions into the materials in the samples during the deposition can not be ruled out, although it should be noticed that the sticking coefficient of Ar is very low. In any case, this incorporation, if any, should not be very significant, at most down to the detection limit of the RBS technique (<1 atom%). As described in the article, the RBS spectra of the sample with the lowest N flow could be perfectly fitted assuming a 100 atom% pure Cr composition with no extra contamination. It is true that, as pointed out by Hoffmann, the layered samples may deteriorate with time, mostly due to loss of adhesion and chipping as a consequence of the high intrinsic compressive stresses generated during the deposition. In order to minimize these effects and improve the temporal stability of the samples, we kept the thickness of the layers below 1.5 micron. These samples were deposited in the beginning of 2004 and until today no signs of delamination or degradation were observed. Regarding the TiN coating, the sample was provided by Ceratizit.<sup>8</sup> Though it can not be described as a CRM, this company has a precise procedure and is confident in providing the correct values of composition, thickness, density, *etc.* in a reproducible

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manner. Ceratizit is also certain on the lateral homogeneity, a very important parameter for samples to be used in calibration procedures in a destructive method as GDOES. As indicated by Hoffmann,<sup>4</sup> Fig. 3 and 4 show the very good homogeneity and the reproducibility of the intensity measurements. There are no intensity error bars missing in Fig. 4, as for the samples where no bars are shown the errors are smaller than the size of the circle.

The determination of the density of the  $\text{CrN}_x$  was made using an algorithm of the HJY instrument software, but it was not the intention of the article to present it as a new method to assess the density. As Hoffmann indicates, this is the best way to proceed when no direct method of density determination is available. The basis of the algorithm is described in the paper of Payling *et al.*<sup>9</sup> In short, the main idea of an algorithm is that in the sample there are pure elements and compounds with their own density. At the beginning only the concentration of pure elements is considered. Using this information along with electronegativity data of elements, the algorithm looks for compounds of them. The selected compounds are subsequently introduced in the density equation as individual entities. The algorithm works fine for metals and nitrides but has important errors in the determination of oxide and carbides densities. In our case, a linear relation of the  $\text{CrN}_x$  density with the nitrogen content was found (density ( $x$ ) =  $7.16 - 1.36x$ ). Using this equation we have recalculated the density value for the stoichiometric  $\text{CrN}_{x=1}$  to be  $5.80 \pm 0.07 \text{ g cm}^{-3}$  which compares well with the value found in the literature of  $5.90 \text{ g cm}^{-3}$ .

Despite these approximations and the potential improvements that can be applied to the proposed method, the agreement of the quantified GDOES profiles on nitride coatings with other analytical results is, in the opinion of the authors, very promising. The XPS results on the  $\text{TiSiN}_x$  coating gave a composition of 10 atom% Si and 42 atom% N while, after the calibration, the GDOES analysis of that sample gave a 10 atom% Si and 48 atom% N at a depth of 100 nm. The lower nitrogen content measured by XPS is related to a higher oxygen contribution, as XPS mainly probes the outmost surface of the layer. The results obtained on CrN and AlN coatings after comparison

with XPS and RBS results are within the estimated accuracy of 5–10 atom%. Even after recalibration procedures the accuracy in the nitrogen quantification remained in that range. Furthermore, the nitrogen calibration has been also tested on commercial nitride coatings deposited by Balzers (one of the most important coating companies in the world). The results of these GDOES quantitative profiles have been recently published.<sup>10</sup> The authors would like to point out that, although the accuracy obtained for all the samples measured was in the range of 5–10 atom%, the reproducibility of the measurements is, obviously, much better.

The authors have tested the calibration in a wide range of nitride samples (home-deposited and commercial coatings) and, within their expertise, the method works remarkably well after comparison with well-established surface analysis techniques, such as XPS or RBS. We expect that, if not our previously stated arguments, at least these last practical examples would be enough to dispel any of the “serious doubts about the elaborateness in this article and validity of the conclusions” raised in the Comment.<sup>4</sup>

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