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Extended Abstract of PSA-19

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Dissecting the metallic Fe 2*p* photoemission spectrum

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The metallic Fe 2*p* photoemission spectrum poses strong theoretical and analytical challenges. Its multiplet structure cannot be calculated with existing codes. Peak-fitting has been extremely elusive, with no reports in the literature showing possible peak components. Based on the comparison of the spectra for various iron film thickness, a primary function and a multiplet structure for the metallic Fe 2p spectrum is proposed. The fitting method involved state-of-the-art tools such as simultaneous-fitting and the active background approach. A very interesting finding is that the relative strength of its multiplet components is modulated with film thickness.

1. Introduction

The long standing and rapidly growing relevance of first-row transition metals (iron, in particular) and their compounds in nanotechnological applications invigorates the need for their accurate characterization with X-ray photoelectron spectroscopy (XPS). The great difficulty associated to the peak-fitting analysis of the Fe 2*p* photoemission spectra (which is mentioned in many report) is evidenced by the fact that the first report about the composition of ferrite (together with the associated multiplet structure of Fe 2*p* in Fe^{3+}) assessed through XPS was published only two year ago (2017) [1]. This is despite the fact that the Fe 2*p* core level is one of most studied spectra with XPS. The peak-fitting analysis of the *metallic* Fe 2*p* represents an even stronger challenge: to the knowledge of the authors, there is no published literature reporting it.

The difficulty arises from its dense multiplet structure, which cannot be resolved by eye, and from its very large background signal. Both, the multiplet structure and the background signal, are discussed in this presentation.

2. The multiplet structure of the metallic Fe 2*p* spectrum: the primary signal of Fe 2*p*

We report how it was possible to resolve not only the primary function, but the multiplet structure of the metallic Fe 2*p* spectrum. While analyzing the metallic Fe 2*p* spectrum from iron films of various thicknesses (the experimental details are the same as those described in [1]), we encountered a very interesting phenomenon: the relative intensity of the multiplet components is modulated with film thickness. This allowed for the application of the very powerful simultaneous peak-fitting method, through which it is possible to robustly resolve overlapping peaks [2].

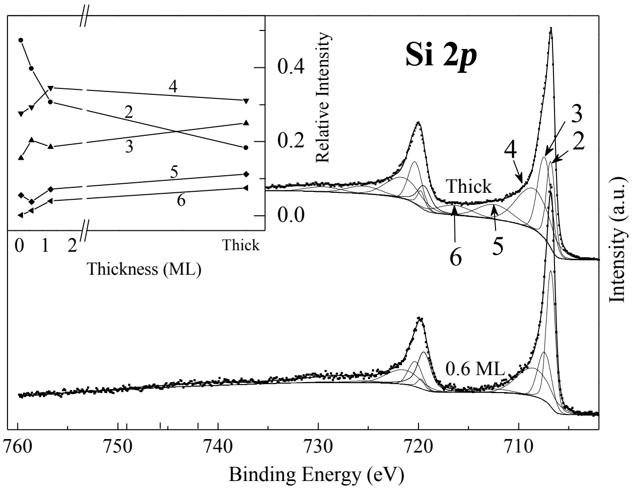

Fig. 1 Fe 2*p* spectra from metallic iron from a) a thick and b) a thin (0.6 ML) film. The lower inset shows the thickness dependence of the various component of the multiplet structure.

It also required the use of state-of-the-art background-modeling tools: we employed a combination of SVSC (Shirley-type) [3] and Slope [4] backgrounds under the active approach [3]. Figure 1 shows the multiplet structure for a thick and thin metallic iron layer on Si(001), and the inset the modulation of the various components with thickness. The smooth behavior of all the components suggest that the hypothesis that the multiplet components are the same for the various films, but with intensities modulated by thickness, holds.

Both the Slope and the SVSC parameters are also modulated with Fe film thickness. It is very interesting that the SVSC parameter, i.e., the Shirley-part of the background, does not vanish as the thickness decreases. The sum of the SVSC and Slope background signals corresponds to three of the four components of the total signal described in Section 4.

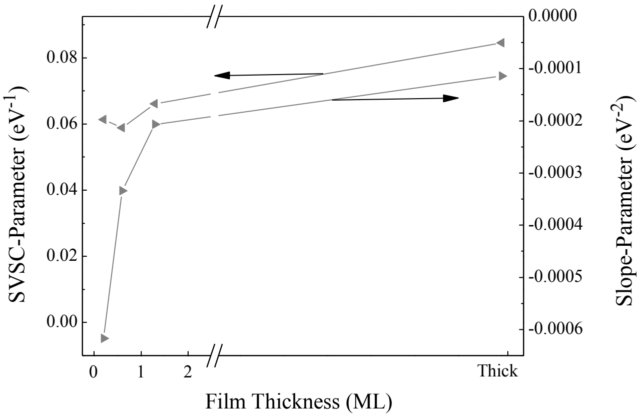

Fig. 2 Dependence of the SVSC and Slope parameters with film thickness. These parameters are obtained from fitting the data similar to that shown in Fig. 1.

3. The early oxidation state of iron

The primary signal for the metallic Fe 2*p* spectrum corresponds to the signal above the background. With the primary signal in hand, it is possible to calculate composition and, as mentioned in Section 4, the inelastic part of the background. We calculated the composition of the oxide that is formed as the metal is exposed to oxygen, which resulted in Fe_2O_3. The fact that this is the expected composition of iron oxide formed at room temperature, strongly suggest that the assessed primary signal, which area plays a fundamental role in the calculation of the top surface oxide, is quantitatively correct.

4. The total signal

As discussed in [5], besides the background due to inelastic scattering, there is an extra signal with its own cross section. This signal is related to the Shirley background. However, it is actually not shaped as the Shirley method describes, which is based on the convolution of the primary signal with a step function. The shape is more complex because it eventually disappears at few tens of eV higher BE, where the inelastic background (i.e., the Tougaard background [6]) meets the total signal. This causes the negative values of the Slope parameter. To be more general, the extra signal is called I_{ORP} to make reference to the off-resonant participator photoemission process proposed in [5] as its physical origin.

In this way, the total signal is composed by the primary signal, its associated inelastic background, I_{ORP} and the inelastic background signal associated to I_{ORP}. In this presentation we describe each one of these components. The background signal in photoemission spectra caused by inelastic scattering is usually calculated by convolving the total signal with the electron-energy loss-function. This method, which was proposed by Tougaard and Sigmund in their classic 1982 paper [6], only works (as clearly indicated in [6]) for homogeneous materials. However, the method is commonly applied to finite thickness films.

In this paper it is also going to be described the proper way to remove the inelastic background signal of spectra from thin-conformal layers including buried layers and delta-doping [7].

5. References

[1] M. Bravo Sanchez, J. A. A. Huerta-Ruelas, D. Cabrera-German, and A. Herrera-Gomez, *Surf. Interface Anal.*, vol. 49, no. July, pp. 253–260, 2016.
[2] J. Muñoz-Flores and A. Herrera-Gomez, *J. Electron Spectros. Relat. Phenomena*, vol. 184, no. 11–12, pp. 533–541, 2012.
[3] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, and M. O. O. Vazquez-Lepe, *Surf. Interface Anal.*, vol. 46, no. 10–11, pp. 897–905, Oct. 2014.
[4] A. Herrera-Gomez, M. Bravo-Sanchez, F.-S. Aguirre-Tostado, and M.-O. Vazquez-Lepe, *J. Electron Spectros. Relat. Phenomena*, vol. 189, pp. 76–80, Aug. 2013.
[5] A. Herrera-Gomez *et al.*, *Surf. Interface Anal.*, vol. 50, no. 2, pp. 246–252, 2018.
[6] S. Tougaard and P. Sigmund, *Phys. Rev. B*, vol. 25, no. 7, pp. 4452–4466, Apr. 1982.
[7] A. Herrera-Gomez, “The photoemission background signal due to inelastic scattering in conformal thin layers (Internal Report),” 2019.