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Uniqueness plots: A simple graphical tool for identifying poor peak fits in X-ray photoelectron spectroscopy

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ABSTRACT

Peak fitting is an essential part of X-ray photoelectron spectroscopy (XPS) narrow scan analysis, and the Literature contains both good and bad examples of peak fitting. A common cause of poor peak fitting is the inclusion of too many fit parameters, often without a sound chemical and/or physical basis for them, and/or the failure to reasonably constrain them. Under these conditions, fit parameters are often correlated, and therefore lacking in statistical meaning. Here we introduce the uniqueness plot as a simple graphical tool for identifying bad peak fits in XPS, i.e., fit parameter correlation. These plots are widely used in spectroscopic ellipsometry. We illustrate uniqueness plots with two data sets: a C 1s narrow scan from ozone-treated carbon nanotube forests and an Si 2p narrow scan from an air-oxidized silicon wafer. For each fit, we consider different numbers of parameters and constraints on them. As expected, the uniqueness plots are parabolic when fewer fit parameters and/or more constraints are applied. However, they fan out and eventually become horizontal lines as more unconstrained parameters are included in the fits. Uniqueness plots are generated by plotting the chi squared (χ^2) value for a fit vs. a systematically varied value of a parameter in the fit. The Abbe criterion is also considered as a figure of merit for uniqueness plots in the Supporting Information. We recommend that uniqueness plots be used by XPS practitioners for identifying inappropriate peak fits.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a widely used surface characterization technique; it is currently mentioned in approximately 10,000 publications per year [1–3]. XPS uses peak positions and peak shapes to provide the identities and chemical states of the elements at surfaces. Because both the natural line widths of XPS signals and their chemical shifts are on the order of 1 eV, peak fitting is an essential part of XPS data analysis [4,5]. However, peak fitting can be a subjective and challenging exercise [6]. For example, Wepasnick and coworkers fit a C 1s narrow scan from oxidized carbon nanotubes (CNTs) using parameters from two previously published fits [7–9]. In both cases, the overall fits were good. However, the fraction of the carboxyl, C(III) [10], signal in the fits differed drastically: ca. 6% vs. 11.0%.

There are a number of possible pitfalls in XPS peak fitting. These include (i) adding too many unconstrained peaks or fit parameters, often without a reasonable chemical or physical basis for them, (ii) using inappropriate backgrounds, (iii) failing to show the summation of ones fit components, and (iv) failing to demonstrate the statistical quality of one's fit with chi squared (χ^2), the reduced chi squared (χ^{2^*}), the Abbe criterion, etc [11,12]. When too many parameters can vary (float) in a fit, they are often correlated, which means they lack statistical meaning. In XPS, the degree of correlation can be identified through the Hessian matrix, **H**, where parameters are correlated if the mixed partial derivatives of χ^2 (the off-diagonal elements of this matrix) are non-zero [11]. We recently introduced the equivalent width and autocorrelation width as less biased figures of merit for XPS narrow scans [13,14]. These width functions are sensitive to chemical changes in materials.

Spectroscopic ellipsometry (SE) data analysis does not involve peak fitting per se. However, SE and XPS data analysis are similar in that both generally involve fitting multiple components and parameters. In both cases, correlation occurs when a large number of fit parameters are employed. In essence, 'correlation' means

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