

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.

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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/ν), 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, \mathbf{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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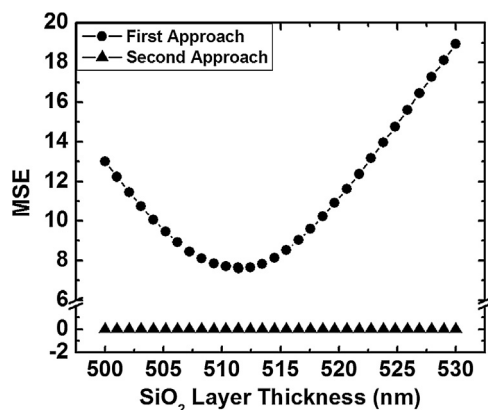


Fig. 1. Uniqueness plots for spectroscopic ellipsometry data showing the MSE (error) as a function of the fixed SiO_2 layer thickness of an Si/SiO₂ sample. The first approach (top, circles) involves reasonable constraints on the fit parameters. In the second approach (bottom, triangles) the fit parameters are unconstrained.

that when a particular parameter varies, other fit parameters can change in a compensatory way, giving the same error to the fit. The SE and XPS communities are well aware of the mathematical calculation of fit parameter correlation, including the parabolic relationship that is often found between chi squared and a given fit parameter [11,15,16]. However, in the SE community, correlation is commonly identified through uniqueness plots, which are graphical tools that can be easily interpreted [17–19].

In a uniqueness plot, the error to the fit is plotted as a function of one of the variables (fit parameters), where this parameter is repeatedly fixed to different values about its optimal value, and the remaining fit parameters are allowed to vary. If the error in the fit rises as the parameter in question is varied, in general in a parabolic fashion [11], the fit is unique. However, if the fit parameter can be systematically varied and the error of the fit stays constant, there is no ‘uniqueness’. That is, if any value of the parameter gives the same result/error, the fit parameter, and therefore fit, are meaningless.

Fig. 1 shows an SE uniqueness plot. It was derived from SE data collected from a ca. 500 nm film of silicon dioxide (SiO₂) on silicon. The data were modeled in standard fashion [20,21] using four layers: (i) the silicon substrate, (ii) an Si/SiO₂ interface layer, (iii) the SiO₂ film, and (4) a roughness layer. In the first approach, reasonable constraints were applied to the model, e.g. the optical constants of the Si substrate were taken from the instrument software and fixed, the thickness of Si/SiO₂ interface layer was fixed and its optical constants were taken from the software, etc. Using this approach, which had a sound chemical and physical basis, the optimal thickness of the SiO₂ layer was found to be 511 nm (see Supporting Information for additional details.) We probed the uniqueness of this result by varying and fixing the thickness of the SiO₂ film about this value (from 500 to 530 nm), recording the mean square error (MSE) of the fit at each constrained value of the thickness. Fig. 1 shows the resulting parabolic uniqueness plot. This plot implies a unique result because the errors increase as we vary the thickness of the SiO₂ layer from its optimal value. That is, we obtain here the favorable result that the other parameters in the model are unable to compensate for forced changes in the SiO₂ film thickness. In a second approach, the model was unconstrained, i.e., all the parameters floated. Fig. 1 shows a non-unique result here – a horizontal line. That is, the same low error is obtained when the film thickness is systematically set to a wide range of values. We conclude that because the error of the fit does not change when the thickness of the SiO₂ layer is varied, the fit has no statistical meaning. Clearly, the uniqueness plots in Fig. 1 constitute a straightforward and useful graphical tool that can aid novice and experienced SE practitioners alike to pinpoint unreasonable fits. Again, a parabolic

result implies uniqueness, while an excessively broad parabola or a horizontal line indicates statistically meaningless results.

Here we propose the use of uniqueness plot to identify inappropriate XPS peak fits. There is a need for this tool because of the increased popularity of the technique – an increasing number of untrained individuals are collecting and analyzing XPS spectra [2,3]. Nevertheless, uniqueness plots should be valuable to inexperienced and experienced practitioners alike. Less skilled users will quickly identify unconstrained, inappropriate models, and those that are more experienced will quickly confirm that their models are more reasonable. Uniqueness plots are most useful in identifying poor peak fits, as opposed to better ones. Of course mathematical fitting alone is an insufficient criterion for the quality of an analysis. Models should always be implemented and constrained based on a priori chemical and physical knowledge about a system and Literature precedent.

To demonstrate uniqueness plots in XPS, we fit two different narrow scans: the C 1s spectrum of an ozone-treated carbon nanotube forest (CNT) and the Si 2p spectrum from an air-oxidized silicon substrate. Here, parabolic plots are obtained when a limited number of fit parameters are employed and more shallow curves, or horizontal lines, when larger numbers of unconstrained parameters are allowed. Both reduced chi squared (χ^2) and Abbe criterion values were explored in these plots. The chi squared-based uniqueness plots appear to be easier to interpret. The Abbe criterion results are reported in the Supporting Information. The uniqueness plot is a standard feature of SE data analysis software. We recommend that vendors of XPS analysis software similarly introduce uniqueness plots. (One of the authors of this paper has already implemented a feature that is somewhat similar to uniqueness plots into a commercial XPS software package [22].) However, special software is not necessary to prepare uniqueness plots. Those shown herein were prepared with our instrument software that does not offer this particular feature.

2. Experimental

Two sets of XPS data were employed in this study:

1. A C 1s narrow scan from an ozone-treated carbon nanotube (CNT) forest with an oxygen content of 3.7 at.% by XPS. This CNT spectrum was collected as part of a study on infiltrated, CNT-templated thin layer chromatography plates [23–25]. Note that this spectrum was taken with an older spectrometer, and that the sample is inherently complex. Accordingly, it is somewhat challenging to resolve/describe all the components in it. A more advanced approach here would probably include accounting for asymmetry in the line shapes and using somewhat different peak widths for the different components per literature reports [26]. Nevertheless, the current fit seems sufficient to illustrate uniqueness plots.
2. An Si 2p narrow scan of a native-oxide terminated silicon shard [27,28] (ca. $1.5 \times 1.5 \text{ cm}^2$). It was air oxidized for one minute at 900 °C in a Thermolyne™ benchtop muffle furnace from Thermo Scientific. The resulting oxide layer was 3.58 nm by SE. The optical constants of Si and SiO₂ for the SE modeling were obtained from the instrument software. Because this spectrum was collected with an older instrument, it was not possible to resolve the $2p_{3/2-1/2}$ doublet. But again, this spectrum seems adequate to illustrate the concepts we introduce herein.

XPS analyses were performed with a Surface Science SSX-100 X-ray photoelectron spectrometer (serviced by Service Physics, Bend, OR) with a monochromatic Al K α source (1486.7 eV) and a hemispherical analyzer. Narrow scans were recorded with a spot size

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