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Comparison of the equivalent width, the autocorrelation width, and the variance as figures of merit for XPS narrow scans

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) is widely used in surface and materials laboratories around the world. It is a near surface technique, providing detailed chemical information about samples in the form of survey and narrow scans. To extract the maximum amount of information about materials it is often necessary to peak fit XPS narrow scans. And while indispensable to XPS data analysis, even experienced practitioners can struggle with their peak fitting. In our previous publication, we introduced the equivalent width (EW_{XPS}) as both a possible machine automated method, one that requires less expert judgment for characterizing XPS narrow scans, and as an approach that may be well suited for the analysis of complex spectra. The EW_{XPS} figure of merit was applied to four different data sets. However, as previously noted, other width functions are also regularly employed for analyzing functions. Here we evaluate two other width functions for XPS narrow scan analysis: the autocorrelation width (AW_{XPS}) and the variance (σ^2_{XPS}). These widths were applied to the same four sets of spectra studied before: (a) four C 1s narrow scans of ozone-treated carbon nanotubes (CNTs) (EW_{XPS}: ~2.11–2.16 eV, AW_{XPS}: ~3.9–4.1 eV, σ^2_{XPS}: ~5.0–5.2 eV, and a modified form of σ^2_{XPS}, denoted σ^{2*}_{XPS}: ~6.3–6.8 eV), (b) silicon wafers with different oxide thicknesses (EW_{XPS}: ~1.5–2.9 eV, AW_{XPS}: ~2.28–4.9, and σ^2_{XPS}: ~0.7–4.9 eV), (iii) hydrogen-terminated silicon surfaces, before and after modification with pentyl groups, and after annealing of the pentyl-terminated surface (EW_{XPS}: ~0.7–1.0 eV, AW_{XPS}: ~1.2–1.6 eV, and σ^2_{XPS}: ~0.12–0.19 eV), and (iv) C 1s narrow scans from five different nanodiamond samples, three of which showed charging (EW_{XPS}: ~2.6–4.8 eV, AW_{XPS}: ~3.8–6.9 eV, and σ^2_{XPS}: ~1.6–4.2 eV). All three of the width functions showed similar trends, except in the case of the C 1s spectra of the CNT samples, which were the most complex spectra evaluated, where σ^2_{XPS} showed poor correlation with the corresponding O/C ratios. Accordingly, we favor EW_{XPS} and AW_{XPS}. EW_{XPS} is advantageous because it is conceptually simple, giving the most intuitive results. AW_{XPS} has the advantage of not requiring the user to specify the height of the function at its maximum, which will be affected by noise. Because these functions are based on different mathematical operations/algorithms, best practices may involve the calculation of both widths for a set of narrow scans. The standard deviation, σ_{XPS}, i.e., the square root of the variance, was also examined. As expected, it gave results similar to σ^2_{XPS}.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is an indispensable analytical tool for surface/material characterization. Indeed, an ISI Web of Science search on the terms ‘X-ray photoelectron spectroscopy’ or ‘XPS’ for papers published in 2013 identified more than 11,000 publications [1,2]. XPS is a quantitative, near surface characterization tool that operates by illuminating a sample with X-rays [3]. The kinetic energies of the photoelectrons generated in the technique are measured by the instrument and converted into binding energies that identify the elements in the sample. XPS spectra are obtained as either lower resolution survey scans or higher resolution narrow scans. Peak fitting is a central part of the analysis of XPS narrow scans because, as noted by Sherwood, the widths of the peaks and the chemical shifts observed for different oxidation states of many elements are often quite similar [4].

In our previous publication [5], we discussed some of the limitations of traditional XPS peak fitting. We noted that while many analysts practice peak fitting with care and competence, the literature also contains many examples of poorly fit narrow scans.

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