Journal of Electron Spectroscopy and Related Phenomena 197 (2014) 93–101

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

On the choice of tuning parameters for use with Robust GCV, Modified GCV and the Discrepancy Principle in the inversion of ARXPS data

D. Peykov[a], R.W. Paynter[b,*]

[a] Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States
[b] INRS Énergie Matériaux Télécommunications, 1650 Lionel-Boulet, Varennes, Québec, Canada J3X 1S2

ARTICLE INFO

Article history:
Received 21 August 2014
Received in revised form
24 September 2014
Accepted 25 September 2014
Available online 8 October 2014

Keywords:
Angle-resolved X-ray photoelectron spectroscopy
Depth profile
Tikhonov regularization
Matrix model

ABSTRACT

Composition depth profiles were extracted from simulated ARXPS data using regularization, with the regularization parameter determined by three different methods (Robust GCV, Modified GCV, and the Discrepancy Principle) that require tuning parameters. For each method, the optimal tuning parameter was determined for two input profile shapes, three Tikhonov regulators (0th, 1st, and 2nd order), and data noise ranging from 1% to 9%. Although universally applicable optimal tuning parameters were not identified, it was found that certain values could consistently produce acceptable results for the input profiles used in this study.

1. Introduction

The recovery of composition-depth profiles from ARXPS data is an ill-conditioned problem [1–3], in which "over-fitting" the noise in the data can cause large and physically unreasonable spikes in the profile. In order to smooth out these irregularities, regularization [1–3] is commonly used, and it seeks an optimal profile that minimizes the "joint function":

$$\min\left\{residual\ norm^2 + \alpha\ solution\ norm^2\right\} \quad (1)$$

Here, the *residual norm*^{2} is the sum of the squared differences between the ARXPS data and the intensities or intensity ratios calculated from the proposed profile. The *solution norm*^{2} is a measure of the lack of smoothness in the proposed profile, and the regularization parameter α is selected to produce the best combination of fitting the data and smoothing the profile.

Recently, we have demonstrated the applicability of the analytical Tikhonov solution [4–6] to the recovery of depth profiles consisting of contiguous line segments from ARXPS data [7]. Subsequently, we reported a comparison of several methods for the determination of an optimal value for the regularization parameter α [8]. Three of these methods required a value for a "tuning parameter" to be provided, and values close to those mentioned in the literature [9] were used following a cursory verification of their effectiveness. In this paper, we report a more thorough investigation into the choice of appropriate values for these tuning parameters, based on mathematical simulations.

Briefly, synthetic ARXPS data were generated from two different input composition-depth profiles, noise was added, and depth profiles were recovered from those data using 0th, 1st and 2nd order regularization, with each of the three parameter choice methods and a range of trial tuning parameter values. The extracted profiles were then quantitatively rated to determine which of the tuning parameter values performed best for a particular combination of method, input profile, and regulator. As the results of any one particular profile extraction are essentially anecdotal, these calculations were performed on 1000 synthetic data sets at each of nine noise levels, ranging from 1% to 9% noise, with the results characterized in terms of medians and inter-quartile ranges.

2. Methodology

An abbreviated presentation of the essential points of the methodology is presented here. The reader is referred to [7,8] for a more complete exposition.

2.1. Intensity model

Rather than investigating the physics of a real measurement, the goal of this study was to seek universally applicable tuning

* Corresponding author. Fax: +1 450 929 8102.
E-mail address: Royston_Paynter@emt.inrs.ca (R.W. Paynter).

http://dx.doi.org/10.1016/j.elspec.2014.09.011
0368-2048/

parameters for three methods of choosing an optimal regularization parameter, and to analyze regularization as a mathematical procedure. To simplify the model and maintain focus on regularization, elastic scattering and surface roughness were not taken into account.

The depth profiles considered consist of linear concentration gradients between n discrete concentration-depth coordinates (c_i, z_i), with z_1 at the surface and a constant concentration c_n in the bulk beyond z_n. The photoemission intensity was calculated from

$$I(\theta) = s\eta\frac{3}{2}\sin^2(\theta+15)\left\{c_1\lambda\cos\theta+\lambda^2\cos^2\theta\sum_{i=1}^{i=n-1}\left(\frac{c_{i+1}-c_i}{z_{i+1}-z_i}\right)\left[\exp\left(\frac{-z_i}{\lambda\cos\theta}\right)-\exp\left(\frac{-z_{i+1}}{\lambda\cos\theta}\right)\right]\right\} \quad (2)$$

in which $I(\theta)$ is the peak intensity at a photoemission angle θ. The counting time, which increases the intensity and reduces the % noise, is quantified by the scale factor s. Other terms include the photoionization cross-section (η), and the photoelectron inelastic mean free path (λ). For simplicity, the solid angle of collection of photoelectrons is taken to be negligibly small, and the analyzer transmission function is assumed to be flat with respect to energy and equal to unity. The value of the photoemission asymmetry parameter was 2 for all peaks and the angle between the incident X-ray beam and the photoemission angle was set to 15° in this basic simulation of a "parallel collection" geometry.

2.2. Matrix-based approach

If the minimization of the joint function is expressed in terms of coefficient and regularization matrices, Eq. (1) takes the form

$$\min\left\{\|I_{noisy}-A\cdot c\|^2+\alpha\|L\cdot c\|^2\right\} \quad (3)$$

in which I_{noisy} is the matrix containing the list of noisy peak intensities at each of the m photoemission angles, and c is the matrix containing the list of elemental concentrations at each of the n depth ordinates in the depth profiles; these concentrations are the variables of the minimization problem. A is the $m \times n$ *coefficient matrix* codifying the physical model of photoemission, Eq. (2), and is defined fully in [7,8]. α is the regularization parameter, which balances the contributions of the residual norm (fitting the data) and solution norm (smoothing the profile), and L is the regularization matrix which was previously defined for 0th, 1st and 2nd order regularization in [7,8].

The analytical solution to (3) is then given by [4–7]

$$c = V(W^TW+\alpha V^TL^TLV)^{-1}W^TU^TI_{noisy} \quad (4)$$

where the superscript T denotes the transpose matrix. This stabilized form of the solution uses the singular value decomposition (SVD) of A (i.e. defining two unitary matrices U and V and a diagonal matrix W, such that $A = UWV^T$).

Eq. (4) provides the global minimum of the joint function without any constraints on the possible values of concentration, which may include very large positive and negative numbers due to noise in the ARXPS data. The subject of this paper is how best to parameterize the Robust GCV (rGCV), Modified GCV (mGCV) and Discrepancy Principle (Disc) parameter choice methods to select the optimal α value, which both minimizes the occurrence of physically impossible negative concentrations and provides the best combination of profile smoothness and data fitting.

2.3. Simulation of noisy data

Noiseless intensity data were generated from the input profiles, Table 1, using the concentration gradient model, Eq. (2), via the matrix calculation $I_{noiseless} = A\cdot(sc)$. The number of profile points (n) was set to 10 with a spacing of 10 Å for Profile 1 and 5 Å for Profile 2. Sixteen photoemission angles (m), evenly distributed between 24.875° and 81.125°, were chosen. The profiles were made up of two elements, oxygen and carbon, as we are primarily interested in the interpretation of ARXPS data obtained on plasma-oxidized hydrocarbon polymer surfaces [10]. Consequently, for a photon energy of 1487 eV, the photoionization cross-sections (η) were taken to be 1 (C 1s peak) and 2.93 (O 1s peak) from the work of Scofield [11]. The photoelectron inelastic mean free paths (λ) were calculated as 36.96 Å (C 1s) and 30.78 Å (O 1s) from the NIST IMFP database software [12], and assumed to be independent of composition.

The input profile for oxygen in Profile 1 was a pseudo-exponential decay from a surface concentration of 32% oxygen to zero concentration at a depth of 60 Å. This profile was used in [7] and [8] and is of particular interest as it is representative of profiles previously investigated experimentally on plasma-modified polystyrene surfaces [10]. The oxygen profile in Profile 2 was a sandwiched layer, centered at 20 Å depth with a FWHM of 15 Å, and equivalent to a profile employed in a recent study of data binning [13]. These two profiles provide a clear contrast in terms of their shapes and in the spacing of their concentration-depth coordinates.

To generate noisy data that obey Poisson statistics [14], each intensity datum in $I_{noiseless}$ was replaced by a random integer taken from a normal distribution with a mean equal to this intensity and a standard deviation equal to the square root of this intensity. This process was used to generate 1000 different sets of noisy data. At each noise level, the same 1000 sets of noisy data were considered with each of three regulators and parameter choice methods. For each parameter choice method, a large number of tuning parameter values were used: 50 values between 0 and 1 for rGCV, 87 values between 0 and 5 for mGCV, and 76 values between 0 and 5 for Disc.

In accordance with previous studies, the % noise was measured on the apparent concentrations, in at.%, rather than on the intensities themselves. For example for oxygen the apparent concentration was calculated as

$$\text{at.\%}(\theta)_{oxygen} = \frac{100(I(\theta)_{oxygen}/\eta_{oxygen})}{(I(\theta)_{oxygen}/\eta_{oxygen})+(I(\theta)_{carbon}/\eta_{carbon})} \quad (5)$$

The equation provided by Harrison and Hazell [14] was used to propagate the noise from the intensities to these apparent concentrations. Since the % noise depends on the value of the intensity, it can be adjusted by carefully selecting the value of the scale factor s. The % noise value used in this paper is one standard deviation of the distribution of apparent concentrations at each angle, expressed as a percentage of the mean apparent concentration at each angle, averaged over the 16 angles.

Finally, when extracting the regularized profiles, 721 values of α were used, chosen to be evenly distributed on a logarithmic scale of α numerically between 10^{-18} and 10^{18} (in the units appropriate to the relevant regulator) for Profile 1 and between 10^{-23} and 10^{13} for Profile 2, to ensure that the calculations ran well into both the over-fitting and over-smoothing branches of the joint function curve, see [8]. The entire range of α values was considered when applying the parameter choice methodologies, including the over-fitted and over-smoothed branches of the joint function curve. All simulations were performed using *Mathematica 9* (Wolfram).