

IUVSTA WORKSHOP

XPS: From Spectra to Results-Towards an Expert System

St Malo, France. April 21-26,2002

Report of Group E

“Reduction of Narrow Scan Data- Chemical Information and Morphology”

Participants: Marie Abel, Thierry Conard, Peter Cumpson, Julia Fulghum, Ulrik Gelius, Stephen Oswald, Luigia Sabbatini, Akihiro Tanaka, Joseph Toth, Wolfgang Unger, Wolfgang Werner.

Topics Discussed:

1. Finding and identifying chemical states
2. Dealing with/getting information on different surface morphologies
3. Getting information on compositional depth profile

1. Finding and identifying chemical states

General procedure for getting chemical information

At all stages make use of all chemical and other prior information (knowledge managed by a very intelligent piece of software, probably the most complex part of the chemical identification procedure)

- (a.) perform binding energy referencing
 - repeat
 - (b.) Qualitative line shape analysis
 - (c.) Quantitative line shape analysis
- until all components have been identified.

(a.) Binding energy referencing

Prior information assumed

- Elemental composition (e.g. from widescan spectra)
- Binding energy scale calibration
- Information on the X-ray source

Prior information desirable

- Does the sample contain C or O other than adventitious?
- Is a Carbon chemical state expected other than C-C bond?
- Is there another preferred element for charge referencing?
- Specimen conductivity?
- Lateral or in-depth surface potential variations expected?

Procedure: use "known" binding energy of a peak present as a reference.

Reference binding energies provided by a database. "Typical" reference peaks:

- adventitious Carbon
- Au peak of a decoration-layer deposited expressly for this purpose
- internal reference using another known peak

Remarks:

- uncertainty in reference BE needs to be known for database comparison
- binding energy scale calibration contributes to error
- uncertainty in apparent binding energy of reference peak contributes to error
- if no chemically well-defined reference peak is used:
take bandwidth of BE's of this peak in the data base as error margin
- if no obvious choice for reference peak:
bandwidth of BE s in data base can be used to select best reference automatically
- need to refer to same C1s binding energy as database

(b.) Qualitative Line Shape Analysis

Prior information assumed

- elemental composition
- x-ray source
- information from database
 - Photoelectron lines as well as chemical states of these
 - Auger lines
 - Satellites
- from database, elemental composition and x-ray source: ghost satellite lines

Prior information desirable

- plasmon satellites and the like (e.g. provided by a simulation based on assumed prior information)

Issues involved in a procedure for qualitative line shape analysis

- peak finding procedure (statistics: when is a peak a peak?)
- classification of intensity of found peaks
- identification of peaks by comparison with data base and/or simulation
- resolving overlapping peaks

Output

- a number of identified peaks with chemical information

(c.) Quantitative line shape analysis

Prior information desirable

- any information helping to constrain the peak fitting procedure to converge to an unambiguous result

Issues involved in a procedure for quantitative line shape analysis

- elimination of X-ray satellites and inelastic background
 - Straight line background (e.g. for a homogeneous insulator where Shirley doesn't work well)
 - Shirley (if it doesn't work use straight line)
 - include the shape of the background in the peak fitting procedure
- methods for peak fit
 - linear least squares fit
 - factor analysis (needs to be developed for shifted peaks)
- peak fit based on
 - synthetic peaks (Gauss, Lorentz, Doniach-Sunjic)
 - empirical reference peaks (own measurements or external database)

Output

- a number of components with position, width, height in case of synthetic peaks
- a number of components with respective relative intensities and position for empirical peaks
- a mixture of these two

Finding and identifying chemical states: summary in form of a decision tree (flowchart)

(a.) Binding energy referencing

- was binding energy referencing performed successfully?
- no: Alert/ and ask user for advice
 - possible action:
 - stop
 - Auger parameter analysis this might eventually imply acquisition of additional scan
 - proceed by using additional spectral features to identify the chemical state based on energy differences rather than on absolute binding energies (satellite or binding energy difference between peaks)
 - proceed without referencing
- yes: proceed with qualitative line shape analysis

(b.) Qualitative Line Shape Analysis

- if all peaks identified: proceed
- if not all, but most peaks identified: alert and proceed

- if the strongest peaks remain unassigned: alert and stop
- inconsistency with prior info: alert and stop
- if all peaks exhibit a similar shape: alert (differential charging) and stop
- if multiple chemical states identified at this stage: flag Theme C

-if at least one round of quantitative lineshape analysis was performed or customer's questions answered: chemical state identification finished

-if not finished: proceed with quantitative line shape analysis

(c.) Quantitative Line Shape Analysis

-if the components are inconsistent with prior information: alert and stop

-if the number of components is changed: proceed with next round of qualitative line shape analysis

-else: done

2. Dealing with/getting information on different surface morphologies

Possible Goals:

a.) Obtain information on morphology

b.) Avoid erroneous data interpretation resulting from effects of morphology

c.) Acquire chemical and/or quantitative information in spite of difficult morphology by using appropriate model

Examples of different surface morphologies:

non ideally-flat topography, roughness, lateral inhomogeneity, islands, nanoparticles, depth distribution of components, separated phases, (extremely) porous surfaces, also known as high-Brunauer-Emmet-Teller (high-BET) surfaces

General considerations:

- all of these cases can be analyzed if the analyzed area is smaller than the typical feature size

- if the feature size is smaller than the analyzed area (the typical case in XPS) the obtainable information is more limited (see table below)

- in general these analyses require additional thought, data acquisition time and attention to data interpretation/quantification

- in terms of quantitative modeling, simple geometric models accounting for influence of morphology on measured spectra have proven to be effective for almost all of the above cases. Suggestion: development of correction factors for some of these cases

- data acquisition at 2 or more angles is qualitatively useful to check some aspects of sample homogeneity (or lack thereof).

Survey of information possible

-For cases where the analyzed area exceeds the feature size, the following table summarizes the possible information that can be gained on such specimens using XPS.

surface	information on morphology parameters from XPS	(quantitative) information on chemistry from XPS
rough	no	possibly
islands	yes	possibly
high BET	yes	possibly
separated phases	in some cases	in some cases
nanoparticles	no	possible
depth distribution	yes	yes

The entries in the table are understood to have the following meaning:

- yes: in principle, yes, but the user needs to be aware that the analysis will require an expert and will be time consuming and costly.
- no: in principle, yes, but there are other analysis techniques that will solve the problem faster, cheaper and more reliably
- possibly: in principle, yes, but the associated error margin may be large and needs an expert to be established
- in some cases: in principle, yes, but not always, depending on the actual situation

Surface morphology: initial diagnostic

- measure more than 1 angle (e.g. 0, 60 degrees)
- if no differences in ratios observed, sample is homogeneous or consists of adjoining phases (on scale of analysis) and standard quantification methods can be applied
- if large variations in ratios are observed, sample morphology will affect quantitative methods (consult expert)
- here it is assumed that an eventual adventitious C overlayer is handled separately

Surface morphology: lateral inhomogeneity

- inhomogeneous surface distribution of chemical or elemental species
- spatial resolution (small area spectroscopy, imaging) must be smaller than the area of inhomogeneity
- use information from customer, optical microscopy to initially assess whether or not XPS analysis is feasible or if another technique should be utilized
- based on length scale required to solve material problem and spatial resolution of instrument warn customer additional time (and money) will be required for proper data collection

Surface morphology: roughness

- for overlayer thickness determination the effects of surface roughness are minimized in the magic angle range of 35-55° w.r.t the surface normal
- outside of this range, errors of 2-10x possible
- homogeneous samples: absolute intensities decrease but intensity ratios unaffected (need to be aware of C contamination)
- quantitation: average slope of micro-features is the appropriate measure for roughness
- charging effects may be worse on rough samples, resulting in line-broadening

Surface morphology: islands

- island formation can be evaluated through angle resolved XPS (ARXPS)
- measure spectral shape, including background, at more than 1 angle
- analysis:
 - ratio spectra
 - QUASES-type analysis
- data analysis generally requires model with initial assumptions about island formation
- possible to disprove a model, but difficult to use a model to determine island size and coverage accurately (correlated parameters)

Surface morphology: high BET surfaces

- catalysts on supports, powdered samples, other porous surfaces
- at BET values > 70m²/g, standard quantification methods can not be used; more sophisticated geometrical models required
- with an appropriate model, information possible on
 - chemistry
 - particle shape/diameter
 - concentration

Surface morphology: nanoparticles

- practical definition: particle diameter of the order of the inelastic mean free path
- morphology best determined by SEM, TEM, etc
- evaluation of chemistry of nanoparticles can be complicated by particle size effects
 - binding energy shifts
 - peak broadening (size distribution?)
- idealized models can generally not be utilized for quantitation
- simple geometric models often work surprisingly well

Surface morphology: depth distribution

- various methods for data analysis available (these are discussed in detail in the next section)
- quantitative analysis requires parameters like the density, cross-sections, AL's
- reproducibility (precision) and identification of differences in sample sets are easier to achieve than absolute truth (accuracy)

3. Getting information on compositional depth profile

Categories discussed

- (a.) homogeneous overlayer on homogeneous substrate
- (b.) multilayers
- (c.) the rest

(a.) Homogeneous Overlayer on Substrate: a single narrow scan was measured

More than one peak of similar KE (e.g. oxide on elemental substrate)

- Ratio of overlayer/substrate peak intensities at a single angle
- C contamination layer can be ignored
- Thickogram, Arctick, etc

One peak available

- e.g. Carbon contamination; ignore C and look at variation in substrate signal
- Substrate peak at 2 angles
- Usual quantitation (peak intensities; exponential attenuation assumption)
- Peak shape analysis (using substrate peak)
- Beware of geometric artifacts

Comments

- determination of thickness does not require more than 1 or 2 angles
- error propagation relatively straightforward
- emission angles of > 60 degrees should not be used
- beware of diffraction effects (check by polar scan if necessary)

Homogeneous Overlayer on Substrate: more than one narrow scan was measured

- use two peaks of same element (different KE)
- use two peaks (overlayer and substrate) with large difference in KE
 - peak intensity ratios
 - geometrical artifacts insignificant
 - need transmission function
 - quantify using peak intensities

Comments

- C contamination layer correction may be required
- variable parameters (density, AL) correlate
- consistency is important in choice of parameters for analysis of data from multiple, related samples

Homogeneous Overlayer on Substrate: Angular Distribution was measured

- measurement of more than one peak of similar kinetic energy
 - the slope of a plot of $\log(I_s/I_o + 1)$ vs $1/\cos(\theta)$ for neighbouring peaks gives the thickness in units of the inelastic mean free path
 - Here I_s/I_o represents the substrate-overlayer intensity ratio and θ is the polar emission angle.
 - quantitation assumptions (ideally flat surface etc.) are probably valid if this results in a straight line
- measurement of a single peak (substrate),
 - a plot of $\log(I)$ vs $1/\cos(\theta)$ gives information on the overlayer

thickness

- peaks of different binding energies
 - a plot of $\log(I)$ vs $1/\cos(\theta)$ for all peaks gives information on the overlayer thickness

(b.)&(c.) Multilayers and the Rest

- more accurate data needed - flag theme A module (more stringent requirements on data acquisition)
- general recommendations: Qualitative stratification (ordering of layers) should come from wide scan analysis
- not more than 5 angles are required (no improvement in depth resolution or accuracy results from additional data)
- Analysis: compare with simulations using available tools (software, experts)