Non-destructive chemical and phase layer profiling of multicomponent multilayer thin ultrathin films

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Abstract. This work covers a method of non-destructive layer profiling of ultra-thin films on solid. The method is based on solution of the problem of elastic and inelastic photoelectron scattering in multilayer inhomogeneous films. An example of depth profiling of an air-oxidized ultra-thin chromium film on a silicon substrate is given.

1. Introduction

Recently, depth profiling of thin films is performed using destructive as non-destructive methods. Standard methods of thin films layer profiling such as secondary ion mass spectrometry (SIMS), transparent electron microscopy (TEM), scanning Auger microscopy (SAM), glow discharge optical emission spectroscopy (GD-OES), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS) and mass spectrometry of laser ablation inductively coupled plasma (LA-ICP-MS) are well developed and widely used in industrial and research laboratories. A survey of various methods of nanometer resolution depth profiling (RBS, SIMS, GD-OES etc.) may be found in [1,2]. However, for non-destructive analysis of thin films, these methods are not good because they are either destructive (i.e. TEM, SIMS, GD-OES) or depth resolution is about or more than the thickness of ultra-thin films themselves (i.e. RBS, SIMS).

One of the non-destructive profiling methods of thin and ultra-thin films is X-ray photoelectron spectroscopy (XPS). Chemical and phase surface profiling is performed by means of XPS. Using standard XPS, relative concentrations are calculated assuming a homogeneous target within all the profiling depth. Real surfaces are always inhomogeneous and multicomponent by depth. Disregarding that leads to significant errors and depreciates the information on elemental relative concentration itself.

As a rule, the near-surface region is not only multilayer but also multicomponent and multiphase. Layer profiling based on photoelectron spectra interpretation from such targets is a complex inverse problem with many unknown parameters. For correct solution of this problem, it is suggested in work [3]: 1) a method of background subtraction considering the difference in energy losses on surface and in bulk; 2) using constant calculation parameters for background and line profile in all the range of photoelectron spectra; 3) using line profile parameters from the spectra of Handbook of X-Ray Photoelectron Spectroscopy [4] for pure homogeneous targets; 4) simultaneous interpretation of different lines of the same element using the same model; 5) a multilayer target model (order of layers) following the history of manufacture and further “life” of the target.

To reconstruct a layer profile, it is necessary to know the order of the layers in the target and electron scattering parameters in the layers. For a unique solution of these problems, in this work, it is
suggested to use photoelectron energy losses spectra recorded in a wide range of electron energy losses (about 100 eV) with a high resolution (no worse than 0.1 eV) near the main lines of an X-ray photoelectron spectrum. As there are few main photoelectron lines generated by photoelectrons of different energy (probing depth depends on the initial electron energy almost linearly) and inelastic electron scattering takes place in layers situated at different depths, the order, elemental and phase layer compound will generate a special background for each photoelectron line. In this work, photoelectron energy spectra interpretation will be based on the solution method of the problem of multiple elastic and inelastic electron scattering in solid described in paper [3]. Simultaneous profiling of photoelectron lines generated by non-scattered and elastically scattered electrons and background generated by inelastically scattered electrons for each line enables to find layer chemical and phase profile with a submonolayer accuracy.

2. Non-destructive chemical and phase layer profiling of multicomponent multilayer ultra-thin films

To find the chemical and phase layer compound of a surface, let us solve the following problems consequently: 1) determination of layer thicknesses of a multilayer target on the base of analysis of peaks generated by non-scattered and elastically scattered photoelectrons, 2) background subtraction in a wide range of energy losses considering multiple inelastic scattering in a multilayer inhomogeneous target. These problems are interrelated. A background generated by inelastically scattered photoelectrons depends significantly on the target structure. Solving the background subtraction problem, an elemental layer profile may be obtained.

2.1. The method of layer thickness measurement in the multilayer model

The feature of XPS measurements is that a signal is recorded from an area significantly more than the probing depth. This area depends on focusing and the sighting angle of the energy analyzer and it is about 0.1 mm²; the probing depth is about 10 nm. So the signal will be inevitably averaged by the measuring area. This enables to assume by interpretation of XPS spectra that the target consists of few plane layers on a substrate. Each layer is homogeneous and may be multicomponent. Inhomogeneities (islets, interlaminar asperities, inclusions, etc.) are averaged by the layer. Inhomogeneity will be described by relative concentration of one or another phase of elements. For each layer, its integral and differential scattering parameters are defined. As far as inelastic scattering differs in bulk and on surface of each layer, let us select a very thin near-surface plane-parallel layer of a thickness \( d_s \), in which energy losses are determined by the losses for surface plasmon excitation. In this near-surface layer, the probability of photoionization is negligible. Out of this layer, the energy losses are losses for bulk plasmon excitation and ionization losses.

Let us develop the calculation method for thicknesses in the multilayer model in approach described in [5–7]. Flux density \( q(z) \) of photoelectrons produced at a depth \( z \) with an energy \( E_0 \), escaped from the target at an angle \( \theta \) to the surface normal and not having lost energy will be determined by the formula

\[
q(z) = n \omega(\gamma) \exp\left( -\frac{z}{\lambda \cos \theta} \right),
\]

(1)

where \( n \) is the atomic concentration; \( \omega(\gamma) \) is the differential cross-section of photoelectron production, \( \gamma \) is the angle between directions of the incident photon and the escaped photoelectron. To find the flux density of photoelectrons escaped from a homogeneous layer of a thickness \( d_s \), it is necessary to integrate expression (1) over all the layer:

\[
Q(d_s) = \int_0^{d_s} q(z) \, dz = n \omega(\gamma) \lambda \cos \theta \left( 1 - \exp\left( -\frac{d_s}{\lambda \cos \theta} \right) \right).
\]

(2)
Let us introduce notations $T_i = \exp(-d_i/\lambda \cos \theta)$, $Q_i^\infty = n \omega(y)\lambda \cos \theta$. Then (2) is written more compactly: $Q_i = Q_i^\infty (1 - T_i)$. The value $Q_i$ is proportional to the intensity $j_i$ of the peaks generated by non-scattered and elastically scattered photoelectrons.

\[
\begin{align*}
Q_{i,N} &= Q_i^\infty (1 - T_i)T_{i+1} \cdots T_N, \\
Q_{N} &= Q_N^\infty (1 - T_N), \\
Q_{N-1} &= Q_{N-1}^\infty (1 - T_{N-1})T_{N-2} \cdots T_N, \\
Q_{0,N} &= Q_0^\infty T_{1} \cdots T_N.
\end{align*}
\]

The layer thicknesses $d_i$ can be found from this system of equations. For that let us divide $Q_{i,N}$ (the flux density of photoelectrons produced by the $i$-th layer) by $Q_{0,N}$ (the flux density of photoelectrons produced by the substrate). This relation will equal to the relation of corresponding peak intensities

\[
\frac{j_i}{j_0} = \frac{Q_i^\infty (1 - T_i)}{Q_0^\infty T_{1} \cdots T_i}.
\]

Let us introduce $f_i = Q_i^\infty j_i/(Q_0^\infty j_0)$. Then Eq. (5) will transform to an iteration formula

\[
\frac{1}{T_i} = f_i \cdot T_{i+1} \cdots T_N + 1 = \frac{f_i}{f_{i+1} + \cdots + f_i + 1} + 1.
\]

Then using the notations and functions above we will use a simple formula for the depth of each layer.

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**Figure 1.** Diagram for derivation of the calculation formula for layer thicknesses
$$d_i = \hat{\lambda}_i \cos \theta \ln \left( \frac{j_i / \omega_i (\gamma) \hat{\lambda}_i}{\sum_{k=0}^{k+1} j_k / \omega_k (\gamma) \hat{\lambda}_k} + 1 \right).$$  \hspace{1cm} (7)$$

2.2. \textit{XPS background subtraction method considering multiple inelastic scattering in a multilayer inhomogeneous target}

Let us find a method for XPS background subtraction considering multiple inelastic scattering in a multilayer inhomogeneous target. The method is based on the solution of the problem of multiple inelastic photoelectron scattering in a multilayer plane-parallel target.

For a photoelectron produced at a depth $z$ with an energy $E_0$ and escaped from the target at an angle $\theta$ to the surface normal be fixed by an energy analyzer with an energy $E$, it should pass a path

$$\cos \theta \left( \frac{z}{\cos \theta} \right) = \Delta,$$

where $T(\Delta,u)$ is the inelastic transmission function of electrons by a layer of material considering multiple inelastic electron scattering.

The total flux density $Q(\Delta)$ of photoelectrons escaped from the target

$$Q(\Delta) = \int_0^\infty q(z,\Delta)dz = n \omega(\gamma) \lambda \cos \theta G(\Delta),$$

where $G(\Delta) = \int_0^\Delta T(u,\Delta)du$, $\lambda = 1/n \sigma_{in}$ is the inelastic mean free path, $\sigma_{in}$ is the inelastic scattering cross-section.

Let us introduce a function $L(\Delta)$ orthogonally inverse to the function $G(\Delta)$ so that the following equation is valid:

$$\int_0^\Delta G(\Delta-\varepsilon)L(\varepsilon)d\varepsilon = \delta(\Delta),$$

where $\delta(\Delta)$ is the Dirac delta function. Then denoting $Q'(\Delta) = Q(\Delta)/Q(0)$, we get from (9)

$$Q'(\Delta) - \int_0^\Delta Q'(\Delta-\varepsilon) \left( \delta(\varepsilon) - L(\varepsilon)/L(0) \right) d\varepsilon = \delta(\Delta).$$

The delta function determines particles that haven’t lost energy. The integral item of the equation describes the flux density of multiply inelastically scattered photoelectrons. The XPS background is generated by electrons multiply inelastically scattered in the material. The $Q'$ function is proportional to $j(E)$, the experimentally measured photoelectron flux of the energy $E$, then let us write a formula for background subtraction following (11):

$$B(E) = A \int_{E_{min}}^{E} j(E') x_b(E - E')dE'.$$

Here $x_b(\Delta) = \delta(\Delta) - L(\Delta)/L(0)$, the value $A$ is calculated specifying background by the energy $E_{min}$. 

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As far as there are no limitations imposed on the target, Eq. (12) determines the procedure of background subtraction for a target of any structure. If a semi-infinite homogeneous target is considered, the Tougaard formula will be derived [9].

3. Results and Discussion
In this investigation, an air-oxidized ultra-thin chromium film 5 nm thick on a silicon substrate was studied. The film was sputtered by magnetron using an experimental setting Leybold Univex 450. The film thickness was controlled with a quartz balance during the sputtering process.

The X-ray photoemission spectroscopy (XPS) studies of the samples surfaces were performed with the help of the electron-ion spectroscopy module based on Nanofab 25 (NT-MDT) platform. In the analysis chamber an ultrahigh oil-free vacuum about $10^{-6}$ Pa. The X-ray source SPECS XR 50 without a monochromator with Mg anode as the X-ray source (1253.6 eV photon energy) was used. The spectra were recorded with an electrostatic hemispherical energy analyzer SPECS Phoibos 225. The energy resolution based on the full width at half maximum (FWHM) of the spectrometer at the Ag 3d5/2 line (peak) was 0.78 eV for non-monochromatic X-radiation Mg Kα. The energy positions of the spectra were calibrated with reference to Cu 2p3/2 (binding energy 932.62 eV), Ag 3d5/2 (368.21 eV) and Au 4f7/2 (83.95 eV) peaks. All survey spectra scans were recorded at a pass energy of 80 eV. The detailed scans of strong lines were in most cases recorded as wide as needed just to encompass the peak(s) of interest and were obtained with a pass energy of 20 eV.

To analyse composition and chemical bond, XPS line of an element of interest needs to be decomposed into component peaks. XPS line structure can be quite complex due to superposition of peaks of the element in its different chemical bond states and presence of satellite peaks. Moreover, shape and width of the peaks could be affected by various factors. For XPS peaks deconvolution, we followed the approach presented in [3]. The background was subtracted according to (12) within a wide range of energy losses.

The depth profile calculation procedure was divided into two stages. At the first stage, the background was calculated by the Shirley method. Then the deconvolution procedure was performed for photoelectron line decomposition into partial peaks. With the help of the calculated partial peak intensities, layer thicknesses were calculated according to (7). At the second stage, the background was calculated by Eq. (12) and the previously calculated layer profile. Then deconvolution procedure
and layer thicknesses were calculated under Eq. (7). As a result of these stages, the final layer profile was calculated. In Fig. 2, the result of calculation by the suggested method is shown. Table 1 shows the layer profile of an air-oxidized chromium ultra-thin film.

Table 1. Chemical and phase depth profile of an air-oxidized ultra-thin chromium film

| Subst. | SiO₂ | 2.6 |
|-------|------|-----|
| 1     |      |     |
| 2     | CrSiOₓ | 1.2 |
| 3     | Cr   | 0.8 |
| 4     | CrO  | 1.8 |
| 5     | CrO₂ | 2.4 |
| 6     | CrO₃ | 0.8 |
| Formula | d (nm) |

4. Conclusion

The suggested method is developed from the new method [3] enabling depth profiling with a submonolayer accuracy, based on analysis of XPS peaks of non-scattered and elastically scattered electrons and relying on the model of a multilayer target resulting from the history of generation and further life of the target. In the suggested method, order of layers in a target will be determined by analysis of peaks generated by multiple inelastic photoelectron scattering. Such approach will increase reliability and accuracy of chemical and phase layer profiling of multilayer multicomponent ultra-thin films.

The suggested method can be implemented using standard X-ray photoelectron spectrometers.

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