Effect of nanocoating morphology on the signal of X-ray Photoelectron Spectroscopy

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Abstract. The paper considers the application of the traditional X-ray photoelectron spectroscopy (XPS) methodology: the Overlayer Thickness Determination for the analysis of coating parameters. In particular situations considered in this work, it is energetically favorable for the atoms of the coating to form clusters, but not be evenly distributed on the surface of the substrate material. The change in the XPS signal is analyzed in situations when the coating is not a plane-parallel homogeneous layer, but an island (cluster) structure. The mathematical model of the XPS signal formation is considered for the case of the cluster covering in the form of parallelepipeds. Photoelectron path distributions (in the coating material) analysis indicated a strong dependence of the signal on the viewing angle. For the purpose of analysis, experimental spectra were obtained for several samples: gold depositions of various thicknesses on a silicon substrate. The spectra were measured for different viewing angles of photoelectrons and interpreted within the Straight Line Approximation (SLA). It is shown that proposed simplest model of an island coating allows to describe the effect of a decrease in the value of the effective average coating thickness, determined in plane-parallel geometry, with an increase in the viewing angle, observed in XPS experiments with angular resolution.

The paper presents the results of theoretical and experimental studies of coatings thicknesses ranges from units to fractions of angstrom, based on XPS Peak Shape Analysis. Direct use of traditional formulas obtained in the Strait Line Approximation [1] can lead to significant errors in determining the coating thicknesses.

Coating thicknesses determination based on X-ray Photoelectron Spectroscopy spectra analysis is a well-established procedure [1]. All methods for determining the thickness are based on formulas obtained in neglect of the processes of elastic scattering of a photoelectron. The influence of elastic processes on the flux density of registered photoelectrons is taken into account by introducing correction factors [2].

In a large number of cases, it is energetically favorable for coating atoms to combine into clusters [3], forming an island coating on the substrate surface. Most often, an island structure is observed if the fluence of the coating atoms is on the order of $10^{16}$ cm$^{-2}$, such an amount can form from one to several monolayers of a homogeneous coating.

We use the SLA method to calculate the intensity ratio of the characteristic peaks of the substrate and coating. For example, in the case of gold coating on silicon, we use peaks: Au4f7/2, Au4f5/2, Si2p3/2, Si2p1/2. The advantage of this choice lies in the proximity of the energies of the photoelectrons that form these peaks.
Let us compare the ratios of Au and Si signals in the case of a uniform gold coating on silicon with a thickness $d$ and islands occupying $s$ ($0 < s \leq 1$) on a unit area and having a height $d/s$, so that the coating volume is the same in both cases.

Consider the first case - a uniform flat cover. The XPS signal of the substrate (material 1), in accordance with [1], is determined by the formula:

$$Q_1(\mu_0, \mu, \varphi) = I_{h\nu} n_1 F_1(\mu, \mu_0, \varphi) \mu l_{in1} \exp\left(-\frac{d}{\mu l_{in1}}\right),$$  \hspace{1cm} (1)

where $I_{h\nu} n_1 F_1(\mu, \mu_0, \varphi) \mu l_{in1}$ – signal intensity of a semi-infinite layer of material 1; $\exp\left(-\frac{d}{\mu l_{in1}}\right)$ – attenuation of a signal in a layer of material 2; $\mu_0$ - cosine on the incidence angle; $\mu$ - cosine of the reflection angle.

The intensity of the layer of material 2 is determined by the formula:

$$Q_2(d, \mu_0, \mu, \varphi) = I_{h\nu} n_2 F_2(\mu, \mu_0, \varphi) \mu l_{in2} \left[1 - \exp\left(-\frac{d}{\mu l_{in2}}\right)\right].$$  \hspace{1cm} (2)

In (1) and (2), the mean free path of electrons $l_{in1}$ in material 1 and $l_{in2}$ in material 2 practically coincide since the energies of the peaks of materials 1 and 2 are chosen so that the difference in energies will be much less than the energies of photoelectrons in the peaks of materials 1 and 2 themselves. Further $l_{in1} = l_{in2} = l_{in}$.

The thickness $d$ of the deposited layer of material 2 will be determined based on the relative intensities of the peaks.

$$f(x) = \frac{Q_2(d, \mu_0, \mu, \varphi)}{Q_1(\mu_0, \mu, \varphi)} = \frac{F_2(\mu_0, \mu, \varphi) l_{in2}}{F_1(\mu_0, \mu, \varphi) l_{in1}} \left[\exp\left(-\frac{d}{\mu l_{in}}\right) - 1\right],$$  \hspace{1cm} (3)

where $d$ is the only unknown quantity.

Let us now consider the case of an island surface coverage. We analyze the unit area of silicon surface, in which $(1-s)$ silicon surface is free and $s$ part is covered with plane-parallel islands of height $d/s$, then formula (3), which determines the ratio of the intensities of the gold and silicon peaks will undergo noticeable changes.

![Figure 1. Island coating structure.](image)

Substrate signal (material 1 - silicon):

$$Q_1(\mu_0, \mu, \varphi) = s I_{h\nu} n_1 F_1(\mu, \mu_0, \varphi) \mu l_{in} \exp\left(-\frac{d}{\mu l_{in}}\right) + (1-s) I_{h\nu} n_1 F_1(\mu, \mu_0, \varphi) \mu l_{in}.$$  \hspace{1cm} (4)

Coating layer intensity (material 2 - gold):

$$Q_2(d, \mu_0, \mu, \varphi) = s I_{h\nu} n_2 F_2(\mu, \mu_0, \varphi) \mu l_{in} \left[1 - \exp\left(-\frac{d}{\mu l_{in}}\right)\right].$$  \hspace{1cm} (5)

The relative intensity of the peaks for island coverage will lead us to the formula:

$$f_1(x, s) = \frac{Q_2(d, \mu_0, \mu, \varphi)}{Q_1(\mu_0, \mu, \varphi)} = \frac{F_2(\mu_0, \mu, \varphi) n_2}{F_1(\mu_0, \mu, \varphi) n_1} \frac{s(1-\exp(-\frac{x}{l_{in}}))}{s + (1-s) \exp(-\frac{x}{l_{in}})},$$  \hspace{1cm} (6)

where $x = d/\mu l_{in}$. 

\[2\]
Figure 2. Dependence of the intensities ratio for the signals of the coating and the substrate on $x = 2d/\mu l_{in}$; $f(x)$ – corresponds to a uniform flat coating, $f1(x)$, $f2(x)$, $f3(x)$ – to an island structure, where $s = 0.7, 0.5, 0.35$.

Figure 2 is for the case of registration of photoelectrons along the normal to the target ($\mu = 1$). One should not use formulas (4) and (6) for other viewing angles. But formula (3) is valid at any angles of registration of photoelectrons. Let us show this in figure 3, where it can be seen that with an increase in the registration angle, the path of a photoelectron can pass not through one island of the coating, but through two, three or more. With an increase in the observation angle, the distribution of photoelectrons over the paths in the coating material in the case of an island coating ($s < 1$) and a uniformly distributed homogeneous layer ($s = 1$) approach each other.

Figure 3. The path of the photoelectron depending on the angle of registration: (a) Photoelectrons trajectories emitted from the sample at different angles (SLA model). (b) Distribution of $\varphi(s)$ over the path lengths of photoelectrons in the coating as a function of the surface location of the photoelectron exit point: 1 - uniform coating with thickness $d$; 2,3,4,5 - exit from the island structure (formula 6), respectively, along the normal to the surface ($\theta = 0$) and at the angles $\theta_1, \theta_2, \theta_3, \theta_4$. 

\[ (0.1, 0.5, 0.7, 0.9) \]
XPS measurements of submonolayer coatings of gold on silicon were carried out on two installations: on the SPECS installation in the AIC laboratory (Analytical Instrumentation Center) at the Vienna Technical University (TU Wien) with an energy analyzer capable of recording XPS spectra of photoelectrons emitted in the angular range from 27 to 75 degrees, and (B) on the KRATOS installation in the angle resolved mode - rotating the target to register XPS spectra at angles close to the normal and angles that are about 70° with the normal.

Figure 4. Gold layer coatings thickness values measured on the SPECS installation.

The experimental data processing was carried out on the basis of the methods presented in the works [4–6]. Calculations consistently showed a decrease in coating thickness values with an increase in the viewing angle relative to the normal. Similar measurements of the thicknesses of plane-parallel, uniform coatings led to the thickness values independent of the viewing angle.

Figure 5. Gold layer coatings thickness values measured on the KRATOS installation.

The observed effect is described on the basis of a parallelogram island coverage model. This model made it possible to observe the change in the Path Length Distribution Function (PLDF) of the emitted photoelectrons depending on the viewing angle. PLDF determines the intensity ratio of the coating and the substrate XPS signals.
Results obtained indicate that a series of experiments with angular resolution should be carried out to determine the average effective coating thickness. The value of the critical viewing angle, after which the thickness value is stabilized, is determined by the density distribution of the islands \( s \).

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