Investigation of monolayer and submonolayer films using X-ray photoelectron spectroscopy

V P Afanas’ev1, D N Selyakov1, O Yu Ridzel2, M A Semenov-Shefov1 and A N Strukov3

1 National Research University «Moscow Power Engineering Institute», 111250, Russia, Moscow, Krasnokazarmennaya 14
2 Schlumberger Moscow Research SMR, 125171, Russia, Moscow, Leningradskoe shosse 16A/3
3 The Southwest State University (SWSU), 305040, Russia, Kursk, 50 Let Oktyabrya 94

E-mail: v.af@mail.ru

Abstract. A method of layer thickness determination by X-ray photoelectron spectroscopy (XPS) is analyzed. Angle-resolved XPS spectra measured for three samples (gold films of different thicknesses located on top of silicon substrates) have been interpreted by the straight line approximation (SLA) model. Two configurations of films were considered: (i) a flat surface of a semi-infinite layer (substrate) is covered with a flat homogeneous layer, (ii) coating constitutes an island (cluster) structure. It is shown that the simplest model of an island coating makes it possible to qualitatively explain the effect of decreasing of the effective average coating thickness observed in the angle-resolved XPS experiments.

1. Introduction

Overlayer thickness determination is an important application of X-ray Photoelectron Spectroscopy (XPS).

This technique is based on measurements of elastic peaks formed by the photo-electrons emitted from inner shells of atoms related to a substrate or a film. We assume the presence of a plane-parallel film on a semi-infinite flat substrate [1]. The model presented in [1] is based on the straight line approximation (SLA), which completely ignores elastic scattering processes and takes into account only inelastic scattering of photo-electrons while the elastic scattering cross section is comparable with the inelastic cross section and sometimes exceeds it. A consistent method describing an XPS signal and considering all the circumstances arising during the transport of a photo-electron in the plane-parallel geometry of a multilayer target was presented in [2]. A detailed and more accurate information on the film thickness obtained by the XPS technique provides an opportunity for reliable determination of the stopping power of light ions with keV energies in various materials [3] from experimental data on the reflection functions of light ions for multilayer targets [4, 5]. At present, the variability of experimentally determined values of the stopping power in gold for 10 keV energy ions presented in the Andersen and Ziegler tables [6] constitutes hundreds percent.
In this paper we will consider how the XPS signal changes if the film is not a flat homogeneous layer but constitute an island (cluster) structure, which is energetically favorable for gold atoms of the film. Such structures are typical for gold in submonolayer configurations [7].

2. Films investigation by traditional XPS methodology
Consider the simplest model: a flat surface of a semi-infinite layer (substrate) made of material 1 (silicon), covered with material 2 (gold) in two configurations: the first is a flat uniform coating, the second is the coating formed by the same amount of material as in the first case but as a set of parallelepipeds. The uniform and cluster coatings of the samples are shown in figure 1.

![Figure 1. XPS experiment geometry (a), flat homogeneous coating (b), island (cluster) coating (c).](image)

Consider the first configuration – a uniform flat cover. The XPS signal of the substrate (material 1) according to [1] is determined as follows:

\[ Q_1(\mu_0, \mu, \varphi) = I_{hv} n_1 F_1(\mu, \mu_0, \varphi) \mu l_{in1} e^{-d \mu l_{in1}}, \]  

(1)

where \( I_{hv} n_1 F_1(\mu, \mu_0, \varphi) \mu l_{in1} \) is the signal intensity of a semi-infinite layer of material 1, \( e^{-d \mu l_{in1}} \) is the attenuation in the layer of material 2 with a thickness of \( d, \mu = \cos \theta, \mu_0 = \cos \theta_0 \).

The intensity from the layer of material 2 is determined by the following equation:

\[ Q_2(d, \mu_0, \mu, \varphi) = I_{hv} n_2 F_2(\mu_0, \mu, \varphi) \mu l_{in} \left( 1 - e^{-d \mu l_{in2}} \right). \]  

(2)

In (1) and (2) the inelastic mean free path of electrons \( l_{in1} \) in material 1 and \( l_{in2} \) in material 2 are almost equal since the energies of the peaks of materials 1 and 2 are chosen so that the difference in peak energies will be much less than the energies of photoelectrons in materials 1 and 2. Further \( l_{in1} = l_{in2} = l_{in} \).  

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[7] Reference to be added.
The thickness determination of the layer of material 2 will be based on the relative intensities of the peaks:

\[ f(x) = \frac{Q_2(d, \mu_0, \mu, \phi)}{Q_1(\mu_0, \mu, \phi)} = \frac{F_2(\mu_0, \mu, \phi)l_{in}n_2}{F_1(\mu_0, \mu, \phi)l_{in}n_1} \left( e^{\frac{d}{l_{in}}} - 1 \right), \]  

(3)

where \( d \) is the only unknown quantity.

Expression (3) leads to the final formula for the layer thickness determination:

\[ d = \ln \left( \frac{Q_2(d, \mu_0, \mu, \phi)}{Q_1(\mu_0, \mu, \phi)} \times \frac{F_1(\mu_0, \mu, \phi)l_{in}n_1}{F_2(\mu_0, \mu, \phi)l_{in}n_2} \right) \times \mu l_{in}. \]  

(3a)

Let us now consider the configuration of an island (cluster) surface coverage. Analyze the structure when half of the silicon surface covered with plane-parallel islands with a thickness of 2d. Formula (3), which determines the intensity ratio of peaks 1 and 2, will undergo noticeable changes.

Substrate signal intensity (material 1 – silicon):

\[ Q_1(\mu_0, \mu, \phi) = \frac{1}{2} I_{hv} n_1 F_1(\mu, \mu_0, \phi) \mu l_{in} e^{-\frac{2d}{l_{in}}} + \frac{1}{2} I_{hv} n_1 F_1(\mu, \mu_0, \phi) \mu l_{in}. \]  

(4)

Coating layer intensity (material 2 – gold):

\[ Q_2(d, \mu_0, \mu, \phi) = \frac{1}{2} I_{hv} n_2 F_2(\mu_0, \mu, \phi) \mu l_{in} \left( 1 - e^{-\frac{2d}{l_{in}}} \right). \]  

(5)

Then the ratio of the peak intensities leads us to the formula:

\[ f_1(x) = \frac{Q_2(d, \mu_0, \mu, \phi)}{Q_1(\mu_0, \mu, \phi)} = \frac{F_2(\mu_0, \mu, \phi)l_{in}n_2}{F_1(\mu_0, \mu, \phi)l_{in}n_1} \left[ 1 - \frac{1 - e^{-x}}{1 + e^{-x}} \right], \]  

(6)

where \( x = \frac{2d}{\mu l_{in}} \).

Figure 2 illustrates the behavior of the signal intensity ratio for island and uniform coverage \( f(x) \) is the ratio of intensities determined by formula (3), \( f_1(x) \) – determined by formula (6)).

![Figure 2](image_url)

**Figure 2.** Dependence of the intensities ratio for the signals of the coating and the substrate on \( x = \frac{2d}{\mu l_{in}} \); \( f(x) \) corresponds to a uniform flat coating, \( f_1(x) \) – to an island (cluster) structure.
We emphasize that the results presented in figure 2 are typical for the case of detecting photo-electrons at angles close to the surface normal. If the flux of photo-electrons is detected at grazing angles, the curves \( f(x) \) and \( f1(x) \) will coincide. The value of the critical angle at which curves coincidence will be observed will be determined by the shape of the islands. In the model under consideration, we will record the invariability in determining the layer thickness at angles exceeding \( \sim 65^\circ \).

3. Experimental XPS analysis of coatings with developed (island) surface morphology

The presence of an island (cluster) surface coating can be confirmed by XPS measurements with angular resolution. The presence of islands will be accompanied by a decrease in the layer thickness values determined by (3a) as the detecting angles approach the grazing angle. The average value of the film thickness (the thickness of an equivalent homogeneous layer) is determined by detecting the XPS signal at angles exceeding the critical angle determined by the island morphology.

![Figure 3. Au/Si XPS spectra (sample #2) at different detecting angles: 27\(^\circ\), 51\(^\circ\), 75\(^\circ\).](image)

1 – Au4f7/2; 2 – Au4f5/2; 3 – Si2p3/2; 4 – Si2p1/2.

Based on the presented experimental data, in accordance with formula (3A), the equivalent thicknesses of homogeneous gold layers are determined.

The presented experimental data can be interpreted within the framework of the developed simplest model of an island coating (coating with developed morphology). For the first sample, no change in the effective average coating thickness is observed. This is explained and by the fact that \( f(x) \) and \( f1(x) \) curves (fig. 2) coincide for the low values of film thicknesses. The effect of decrease of the effective film thickness vales is observed for the second and third samples and corresponds to the simplest model of XPS signal formation by an island structure presented in this work.

4. Conclusions

The use of traditional XPS technique [1] in order to determine coatings thicknesses is a well-developed method aimed to investigate homogeneous plane-parallel (and multilayer in general case) films with a thickness comparable with the electron inelastic mean free path. High-resolution photoelectron spectroscopy, which makes it possible to determine the structure of clusters from the absorption spectrum in the ultraviolet range, is not considered in this work. The presence of the
clustering effect of the coating material [7] leads to the fact that the coating constitute an island structure. It is shown that the simplest model of the island coating makes it possible to qualitatively interpret the effect of a decrease of the effective average coating thickness observed in XPS experiments with an angular resolution.

**Table 1.** The results of layer thickness determination.

| Sample | Detecting Angle | Au/Si Peak Intensity Ratio | Thickness of homogeneous gold layer $(d/l_{th})$ |
|--------|-----------------|---------------------------|-----------------------------------------------|
| 1      | $27^0$          | 1.26                      | 0.07                                          |
|        | $51^0$          | 2.12                      | 0.08                                          |
|        | $75^0$          | 5.35                      | 0.07                                          |
| 2      | $21^0$          | 8.89                      | 0.39                                          |
|        | $51^0$          | 10.17                     | 0.31                                          |
|        | $75^0$          | 25.88                     | 0.25                                          |
| 3      | $27^0$          | 7.81                      | 0.36                                          |
|        | $51^0$          | 9.76                      | 0.30                                          |
|        | $75^0$          | 18.29                     | 0.19                                          |

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