

THEORETICAL NOTES ON XPS SIGNAL FORMATION AND PROCESSING IN TWO-COMPONENT TARGETS

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Abstract. We present theoretical investigations on the factors playing important role for formation of X-ray photoelectron spectroscopy (XPS) signals from two-component targets. Several cases of different modified layers created during ion bombardment are considered. The concentration distributions and the related XPS-signal profiles are analytically calculated as a function of the depth. Computer simulation (using Monte Carlo methods in terms of the well-known TRIMDYN code) are also presented with the aim of achieving reliable interpretation of the concentration depth profiles obtained by XPS.

1. Introduction

The XPS analysis is generally regarded as the most readily interpretable, informative and essentially nondestructive technique for surface quantitative investigations. The surface analysis methods should provide an adequate information on the surface or interface elemental composition without distortion due to bulk distribution. This requirement plays a decisive role, especially in the studies of preferential sputtering, bombardment-induced segregation and diffusion, etc., taking place under ion treatment of solid surfaces when an altered layer is formed having component concentration different from that of the bulk. What is more, even the composition of an untreated surface is different from that of the bulk because of segregation phenomena.

Various methods have been proposed to solve the problem of extracting information on the in-depth concentration profile [1, 2] based on several limiting assumptions, such as that for an automatically flat surface, or on the requirement for some a priori information on the type of distribution, especially in multilayer samples.

In an attempt to illustrate the influence of the depth profile distribution parameters on the determination of the surface composition, we discuss here several simple depth-profile approximations of an altered interface composition in two-component targets, thus showing the necessity of data processing. In addition, we simulate the profiles

by means of a dynamic Monte Carlo computer code in order to estimate some of the altered layer parameters, while taking into account the real and the observed surface concentrations.

2. Procedure of Estimating the Elemental Ratio

The XPS signal from a two-(and more) component target is proportional to the photoelectron flux emitted from about 5-6 layers beneath the surface [3].

$$I_i(\theta) = k \int_0^{\infty} n_i(x) \exp\left(-\frac{x}{\lambda_i \cos \theta}\right) dx \quad (1)$$

where I_i is the intensity of the photoelectron flux at take-off angle θ due to the i -th component of the target, $n_i(x)$ is the atomic density of the i -th component at depth x , λ_i is the specific inelastic mean-free-path (IMFP), and k is a normalizing proportionality coefficient (k includes the energy dependent transmission function of the analyzer, the photoemission cross-section, etc.).

The following considerations are based on the assumption that the total atomic density is independent from x , at least within the altered layer, so that the atomic density of the components is proportional to the corresponding atomic fraction $c_i(x)$ (the elemental concentration), or $n_i(x) \propto c_i(x)$. Hence,

$$I_i(\theta) = k' \bar{c}_i \quad \text{and} \quad \sum_i c_i(x) = 1 \quad (2)$$

where \bar{c}_i is the elemental concentration as "observed" by the XPS analysis.

Let us expand the dependence $c_i(x)$ in the following form:

$$c_i(x) = c_i(0)\varphi_i(x) + c_i(\infty)[1 - \varphi_i(x)] \quad (3)$$

where $c_i(0)$ and $c_i(\infty)$ are the component concentrations at the surface and in the bulk, respectively, and $\varphi_i(x)$ is the attenuating function — $\varphi_i(0) = 1$, $\varphi_i(\infty) = 0$.

From (2) and (3) we can easily obtain

$$\sum_i [c_i(0) - c_i(\infty)]\varphi_i(x) = 0. \quad (4)$$

For a two-component target, using (2) and (4), we can write

$$\varphi_1(x) = \varphi_2(x).$$

If we denote by n_s the elemental concentration at the surface $n_s = \frac{c_2(0)}{c_1(0)}$, and by n_b , the ratio in the bulk $n_b = \frac{c_2(\infty)}{c_1(\infty)}$, in analogy with the "observed" concentration,

we can introduce an "observed" elemental ratio \bar{n}_s as follows:

$$\bar{n}_s = \frac{c_2}{c_1} = \frac{\int_0^{\infty} c_2(x) \exp\left(-\frac{x}{\lambda_2 \cos \theta}\right) dx}{\int_0^{\infty} c_1(x) \exp\left(-\frac{x}{\lambda_1 \cos \theta}\right) dx}$$

We can finally obtain:

$$\frac{\bar{n}_s}{n_s} = \frac{\lambda_2}{\lambda_1} \frac{1 + A_1}{1 + A_2} \frac{1 + A_2 \frac{n_b}{n_s} \frac{1 + n_s}{1 + n_b}}{1 + A_1 \frac{1 + n_s}{1 + n_b}} \quad (5)$$

where A_i is a function of $\frac{a}{\lambda_i}$, with a being a characteristic distance within the altered layer (Fig. 1); its shape depends on the shape of $\varphi_i(x)$

$$A_i = \frac{1}{\int_0^{\infty} \varphi(t_i) \exp(-t_i) dt_i} - 1 \quad (6)$$

Here $t_i = \frac{x}{\lambda_i \cos \theta}$, $i = 1, 2$.

It is obvious from (5) that the function A_i can significantly distort the observed surface composition. We shall estimate below the discrepancy between the real and the observed distributions.

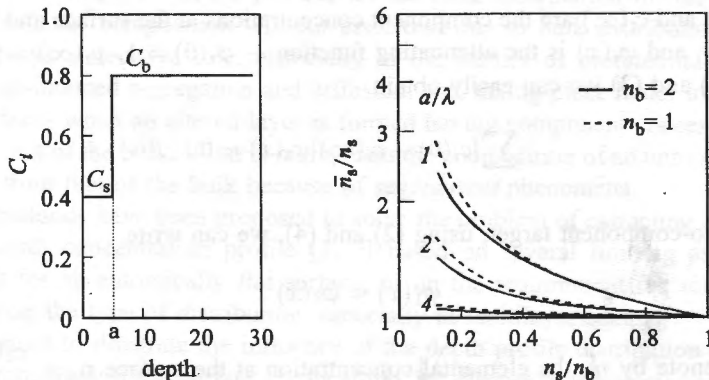


Fig. 1. A step-like distribution

3. Application to Various Depth Profiles

To illustrate the influence of the shape of $\varphi_i(x)$, i. e. of $c_i(x)$, and the characteristic parameter a on the ratio \bar{n}_s/n_s we shall consider some simple examples that may occur in practice. In all cases we shall assume that $\lambda_1 = \lambda_2$.

3.1. Step-like profile

Fig. 1a presents a step-like distribution of $c_i(x)$. From (6) we can obtain:

$$A_1 = A_2 = \frac{1}{\exp\left(\frac{a}{\lambda}\right) - 1}$$

under the conditions:

$$\text{for } 0 \leq x \leq a, c_i(x) = c_i(0), \text{ and for } x \geq a, c_i(x) = c_i(\infty).$$

Fig. 1b shows that for $\frac{a}{\lambda} \geq 2-3$, there exists a wide range of values of $\frac{n_s}{n_b}$, where $\frac{\bar{n}_s}{n_s}$ has admissible deviation $\frac{\bar{n}_s}{n_s} \leq 1.10$.

3.2. Exponential profile

Another shape of $c_i(x)$ further approaching the real elemental distribution has an exponential decrease (Fig. 2a), or $\varphi(x) = \exp(-x/a)$. Then for A we obtain the simple expression $A = \lambda/a$. Acceptable discrepancies between n_s and \bar{n}_s (Fig. 2b) correspond to values of $a/\lambda \geq 6-8$.

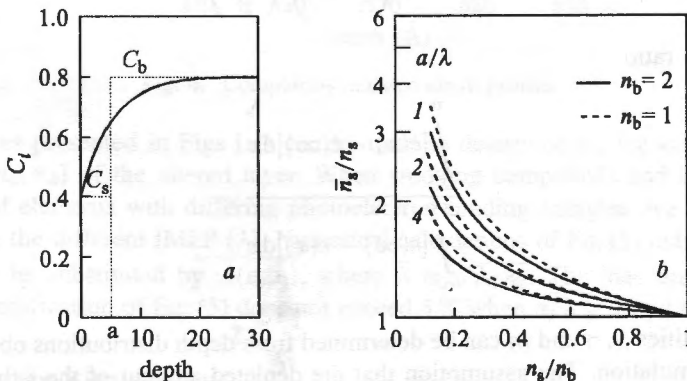


Fig. 2. Exponentially decreasing distribution

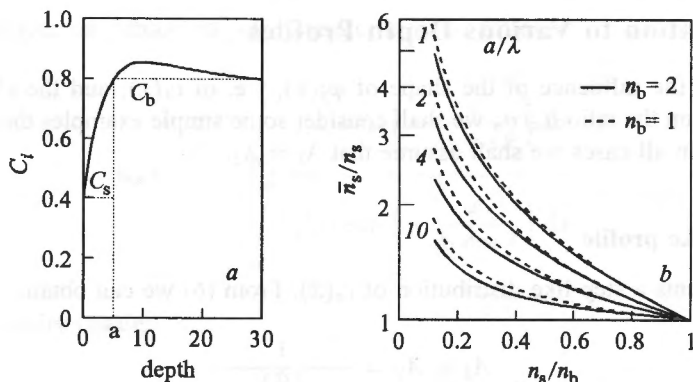


Fig. 3. Double-exponent distribution

3.3. Double-exponent profile

In some practical cases (preferential sputtering, bombardment-induced segregation) the concentration profile can be approximated by a double exponential, especially at saturation (Fig. 3a). For such depth profiles, the analytical form of $\varphi(x)$ becomes

$$\varphi(x) = \frac{\exp(-\beta x) - f \left(\frac{\gamma}{\beta} \right) \exp(-\gamma x)}{\frac{1 - f\gamma}{\beta}}$$

where

$$f = 1 + (1 - m) \left(\frac{\beta}{\gamma} - 1 \right) \left(\frac{f\gamma}{\beta} \right)^{1/(1-\gamma/\beta)}$$

and m is the ratio

$$\frac{\int_0^a [c(x) - c(\infty)] dx}{\int_a^\infty [c(\infty) - c(x)] dx}$$

The quantities β , γ and m can be determined from depth distributions obtained using computer simulation. The assumption that the depleted amount of the i -th component in the depleted layer ($x \leq a$) is equal to its enriched amount in the enriched area ($x > a$) at saturation (steady-state) allows us to simplify the comparison between the experimental data and the computer estimates.

Thus, under the condition $m = 1$, for the function $A(a/\lambda)$ we can write

$$A = \frac{\lambda}{a} \frac{\ln\left(\frac{\beta}{\gamma}\right)}{1 - \frac{\gamma}{\beta}} \left(1 + \frac{\gamma}{\beta} + \frac{\ln\left(\frac{\beta}{\gamma}\right)}{\frac{\beta}{\gamma} - 1} \frac{\lambda}{a} \right).$$

The ratio β/γ and the values of β and γ can be estimated using the value $x = 2a$ and the position of the peak

$$\left(\frac{\beta}{\gamma}\right)^{\frac{\beta/\gamma+1}{\beta/\gamma-1}} = \frac{c(0) - c(\infty)}{c(\infty) - c(2a)}$$

and

$$a = \frac{\ln\left(\frac{\beta}{\gamma}\right)}{\beta - \gamma}.$$

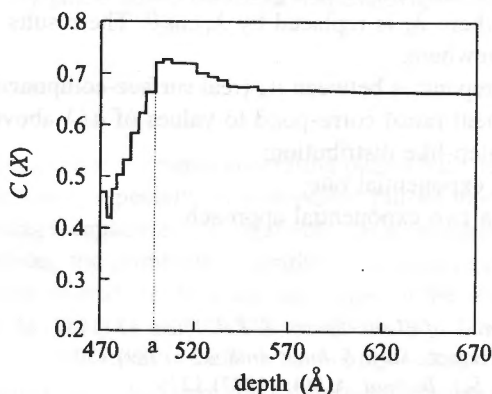


Fig. 4. Computer-simulated depth profile

The curves presented in Figs 1-3 can be used to determine \bar{n}_s for various parameters ($a/\lambda, n_s, n_b$) of the altered layer. When studying compounds and binary alloys consisting of elements with differing photoelectron binding energies, we have to take into account the different IMFP (λ). Numerical calculations of Eq. (5) indicate that A_1 and A_2 can be substituted by $A(a/\bar{\lambda})$, where $\bar{\lambda}$ is $\sqrt{\lambda_1 \lambda_2}$. The inaccuracy resulting from this modification of Eq. (5) does not exceed 5% when $a/\lambda \geq 1$ and $n_s/n_b \geq 0.1$.

4. Computer Simulation

The preferential sputtering of two-component targets, resulting in the formation of an altered layer, can be simulated by using a dynamic Monte Carlo computer code

described elsewhere [4, 5]. The concentration distribution for the case of ZrO_2 is presented in Fig. 4 for a saturation dose of 1×10^{17} ions/cm². The distribution parameters in the altered layer were found to be $n_s = 0.7$, $n_s/n_b = 0.35$, and $a = 34 \text{ \AA}$. Then we calculated $a/\lambda = 1.3$, $\bar{n}_s/n_s = 1.9$; therefore, the value of \bar{n}_s should be expected to be 1.33.

5. Conclusion

The theoretical considerations on the simple depth-profile approximations presented above can be summed up as follows:

- (i) The XPS analysis resolution depends on IMFP (λ), on the characteristic parameter a of the altered layer, and on the elemental concentration ratio on the surface and in the bulk.
- (ii) Combining an analytical approach with computer simulation can be useful in determining the surface elemental concentration, especially in the cases when the characteristic parameter a of the altered layer is comparable with IMFP, and when the solid surface is treated by ion-beam bombardment in surface modification or in layer-by-layer etching for depth-profile determination.
- (iii) The uncertainties inherent to this procedure may be reduced by angle resolved XPS analysis, where λ_i is replaced by $\lambda_i \cos \theta$. The results of such a study will be published elsewhere.
- (iv) Acceptable discrepancies between n_s (real surface-component ratio) and \bar{n}_s ("observed" component ratio) correspond to values of a/λ above:
 - 2–3, for a step-like distribution;
 - 6–8, for an exponential one;
 - 15–20, for a two-exponential approach.

References

1. A. Yih, B. D. Rather. *J. of Electr. Spectr. & Rel. Phen.* **43** (1987) 61.
2. S. Tougaard, H. S. Hansen. *Surf. & Inter. Anal.* **13** (1989) 730.
3. S. Tougaard. *J. Vac. Sci. Technol. A* **5**(4) (1987) 1275.
4. B. Baretzky, W. Moeller, E. Taglauer. *Vacuum* **43** (1992) 1207.
5. H. J. Kang, J. H. Kim, J. S. Kim, D. W. Moon, R. Shimizu. *Surf. Sci.* **226** (1993) 93.