Surface Morphology Characterization using TXRF and SEM

Nikolai V. Alov and Kirill V. Oskolok, Lomonosov Moscow State University, Moscow, Russia

INTRODUCTION
Total reflection X-ray fluorescence spectroscopy (TXRF) is well known as a method of ultramicro, ultratrace and thin-layer analyses based on the effect of total external reflection of primary exciting X-rays [1]. The main advantage of TXRF in comparison with classic XRF is the low detection limit (10^{-6}-10^{-7} mass %). Such element sensitivity is quite sufficient for the determination of trace elements in environmental subjects (ecology) [2] and microimpurities in ultraclean silicon wafers (microelectronics) [3]. However, this advantage can be achieved for plane and smooth sample carriers with low-density only [4]. On the other hand, the hypersensitivity of TXRF to the solid surface roughness is a perspective way for surface morphology diagnosis and the determination of element distribution along the heterogeneous surface. This fact is very important for materials and surface sciences.

It should be noted that there is an approach which distinguishes surface layers with different thickness – monatomic, several atoms and several microns. It is based on the study of the dependence of intensity of the X-ray fluorescence line on the incidence angle of primary X-ray flux (Fig 1) [5, 6]. However, this approach does not permit us to distinguish thin films and three-dimensional islands. Moreover it is correct for low-density subjects semitransparent for incident X-rays only. Hence, the serious problem of the diagnosis of heterogeneous surface morphology (and identification of mechanisms of nucleation and growth of new phase on foreign substrate respectively) by TXRF is not yet resolved.

We propose an alternative approach based on the direct description of conditions of the analytical signal (X-ray fluorescence line) formation on heterogeneous solid surface. The aim of this study was to formulate basic principles of the new approach.

ANALYTICAL SIGNAL FORMATION
In classic XRF, an intensity of the fluorescence line of i-element (I_{XRF}) for a half infinite homogeneous sample is a function of several arguments:

\[ I_{XRF} = k \mu_p, i P_i C_i \]

where \( k = \text{generalized coefficient accounting for the radiation scattering and spectrometer geometry}, \mu_p, i = \text{mass coefficient of primary X-ray absorption}, P_i = \text{fluorescence yield}, I_p = \text{primary X-ray flux}, \text{and } C_i = \text{content of i-element}.

Total external reflection of primary X-rays under grazing angles of incidence (~0.1°) on a sample surface changes the experimental conditions of analytical signal formation considerably. Firstly, nearly the entire spatial separation of fluorescence and primary X-rays leads to substantial growth of the signal to noise ratio in the TXRF spectrum. Secondly, X-ray fluorescence in each atomic layer on a sample surface is excited by both the incident and the reflected primary radiation. Hence, in comparison with classic XRF, the efficiency of excitation of the TXRF spectrum is two-fold on average. Finally, the analysed depth decreases down to ~100 nm during TXRF measurements. This feature causes not only a reduction of the absolute value of the analytical signal but also a more perceptible decrease of the background signal. The lower the analysed depth and the incident angle are, the lower the probability of inelastic scattering of primary and fluorescence radiation and the larger the signal to noise ratio in the spectrum. As a result, the intensity of a fluorescence line for the same half-infinite homogeneous

**BIography**

Nikolai Alov graduated from Lomonosov Moscow State University in 1980 as a physicist and obtained his PhD in 1987 for the investigation of oxygen ion beam-induced surface oxidation of metals. Now he works as a senior research scientist at Lomonosov Moscow State University. His research interests include electron and X-ray spectroscopy and scanning electron microscopy characterization of chemically modified solid surfaces. In addition to research, Dr Alov is a university lecturer on atomic spectroscopy and surface analysis.

**Abstract**

This article describes the influence of heterogeneous surface morphology on analytical signal formation in total-reflection X-ray fluorescence analysis (TXRF). We propose a theoretical consideration of the dependence of X-ray fluorescence lines on the mechanism of new phase nucleation and growth on a foreign low-density substrate. It was found that the analytical signal in TXRF is very sensitive not only to the element composition but also to the different types of surface morphology. The approaches proposed were tested in a combined TXRF and SEM study of the surfaces of disc glass-ceramic carbon electrodes. It was shown that TXRF in conjunction with SEM can be effectively used for the identification of metal and alloy nucleation and growth on solid surfaces.

**Keywords**

total-reflection X-ray fluorescence analysis, analytical signal formation, scanning electron microscopy, electron probe X-ray microanalysis, heterogeneous surface morphology, nucleation and growth mechanisms

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**Author Details**

Dr Nikolai V. Alov, Lomonosov Moscow State University, Department of Analytical Chemistry, 119992 Moscow, Russia.

Tel: +7 095 9392277
Fax: +7 095 9394675
Email:alov@analyt.chem.msu.ru

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layer (d) is equal to the analysed depth (d0) maximum value if the thickness of the phase film, the intensity of the X-ray fluorescence radiation of this phase is excited by X-rays reflected from the ‘phase-substrate’ interface (Fig 2 panel 1), X-rays reflected from the uncovered substrate surface (Fig 2 panel 2) and incident X-rays (Fig 2 panel 3):

\[ I_{\text{TXRF}} = k_1 \cdot I_{\text{TXRF}}^0 \]

where \( k_1 \) = coefficient discounting the relative increase of the signal to background ratio in TXRF spectrum during a simultaneous decrease of total X-ray fluorescence flux.

Analytical signal formation for the heterogeneous phase on a foreign substrate-reflector proceeds in a different way. If the substrate density is less than the phase density (the more widespread case), the condition of primary X-ray total reflection holds for the analysed phase. Therefore, the fluorescence radiation of this phase is excited by X-rays reflected from the ‘phase-substrate’ interface (Fig 2 panel 1), X-rays reflected from the uncovered substrate surface (Fig 2 panel 2) and incident X-rays (Fig 2 panel 3):

\[ I_{\text{TXRF}}^0 = \sum_{i=1}^{n} I_{f,i} \]

Evidently the contribution of component 1 depends on the ‘phase-substrate’ interface area and the thickness of the phase layer. Optimal values of these parameters depend on the phase nature and the energy of primary and fluorescence radiation. If the thickness of the phase layer exceeds the analysed depth, the signal to noise ratio in the TXRF spectrum is reduced as a result of absorption and inelastic scattering of fluorescence radiation in the phase bulk. The contribution of component 2 is proportional to the perimeter of the ‘phase-substrate’ interface, the free substrate surface area and the thickness of the phase layer. Factor 2 promotes not only the increase of the fluorescence line intensity, but mainly primary X-ray scattering and signal to noise ratio reduction. The features of the morphology of the phase surface define the contribution of component 3. This is appreciable on plane or quasi-plane zones of the phase surface that are parallel with the substrate surface. The relative part of such zones (f) depends on the area-mean radius of phase surface curvature (R). It amounts to 100% for uniform thin films (f = 1) and tends to zero for semispherical surfaces (f = 0). In the last case, the efficiency of the primary X-ray scattering and respectively the background signal is high. The heterogeneous surface morphology is determined by the mechanisms of phase nucleation and growth [7]. Below the features of influence of their main varieties on the analytical signal formation in TXRF spectra are reviewed.

Frank-van der Merwe mechanism

The Frank-van der Merwe mechanism involves layer-by-layer two-dimensional growth. The uniform phase film covers the substrate surface. In this case, slight scattering of primary X-rays occurs (f = 1). During the growth of the phase film, the intensity of the X-ray fluorescence line increases gradually. It reaches the maximum value if the thickness of the phase layer (d) is equal to the analysed depth (d0), and finally constant value (d>>d0):

\[ I_{\text{TXRF}} = k_2 \cdot I_{\text{TXRF}}^0 \]

where \( k_2 \) = coefficient discounting the density distribution of i-element in the phase, \( s_{\text{rat}} \) = portion of substrate surface area covered by the phase, \( \mu_f \) = mass coefficient of fluorescence attenuation, and \( \rho \) = phase density.

Volmer-Weber mechanism

The Volmer-Weber mechanism involves three-dimensional island growth. As a rule, the biggest part of the substrate surface is not covered by the phase. Under prevailing lateral growth of three-dimensional nuclei, moderate scattering of primary X-rays occurs (0<f<1). The ultimate intensity of the fluorescence line is finite and less than under thin film formation. It amounts to the maximum value under the increase of lateral growth rate of nuclei (f = 1):

\[ I_{\text{TXRF}} = k_3 \cdot s_{\text{rat}} \cdot \exp(-\mu_f \cdot d) \cdot [k_2-1] \cdot I_{\text{TXRF}}^0 \]

\[ k_3 = \exp(\mu_f \cdot d) - 1 \]

where \( k_3 \) = coefficient discounting a depth distribution of i-element in the phase, \( s_{\text{rat}} \) = portion of substrate surface area covered by the phase, \( \mu_f \) = mass coefficient of fluorescence attenuation, and \( \rho \) = phase density.

Stranski-Krastanov mechanism

The Stranski-Krastanov mechanism involves monolayer(s) plus three-dimensional island growth. The fluorescence line intensity is comparable to the intensity under the layer-by-layer mechanism realization. However the signal to noise ratio in TXRF spectrum is significantly lower.

Thus there are three main mechanisms of the nucleation and growth of new (metal or alloy) phases on foreign substrate surfaces [7]. When the total metal contents are equal, but the metal nucleation mechanisms are different, the intensity of the fluorescence line of the metal in the TXRF spectrum changes significantly. This phenomenon is especially large for phases with thicknesses more than 1 µm, when the relative change of the intensity of fluorescence line is 100 and even 1000-fold (Fig 3). It can be effectively used during ex-situ identification of the nucleation mechanisms in the last stages of the phase formation.

EXPERIMENTAL

We have studied the process of electrochemical formation of new phases – metal and binary alloy – on foreign low-density substrates – inert electrodes. At the same time these plane electrodes played the role of X-ray reflectors during subsequent TXRF measurements of heterogeneous phases. The samples were prepared by the electrochemical deposition and co-deposition of metals from n.10 M (Cu, Pb)(NO3)2 + 0.01M HNO3 solutions on the surfaces of stationary disc glass-ceramic carbon (GCC) electrodes under solution mixing. GCC is an advanced type of glassy carbon with excellent mechanical and electrochemical properties for the electrode preparation for anodic stripping voltammetry. Before metal electrodeposition the surfaces of GCC electrodes were mechanically and electrochemically polished. The electrolysis potential was -1000 mV (silver chloride reference electrode). The electrolysis time was 300 s. The metal electrodeposition technique was described in detail elsewhere [8].

Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) of GCC electrode surfaces were done in a CameBax-microbeam electron-probe microanalyser with an EDX system for element analysis. SEM images of the electrode surface were obtained at magnifications of 100-5000x. TXRF measurements were performed with an Atomika Extra II A spectrometer using MoKα primary radiation. The voltage and current of the X-ray tube were 50 kV and 38 mA respectively. The incidence angle of X-rays was 1.3 mrad [9].

RESULTS AND DISCUSSION

Previously we have studied the process of electrochemical formation of metal (Cu, Cd, Pb), binary and ternary alloy phases on the surfaces of disc GCC electrodes by a number of methods of surface and subsurface analysis – X-ray photoelectron spectroscopy, EPMA, SEM, cyclic
and anodic stripping voltammetry. The total contents of deposited metals and the lateral and depth distribution of metal content in the electrodeposition were determined. The features of the morphology of the electrodeposits, surface morphology and the mechanisms of metal nucleation and growth were described in detail [8, 10]. The results of the analysis of the TXRF spectra were in accordance with data obtained [9].

In particular, the late stages of copper electrodeposition on GCC electrode surface proceeded by the Frank-van der Merwe mechanism. Copper formed a thin film covering the entire electrode surface according to SEM and EPMA data (Fig 4a). Lead electrodeposition proceeded by the classic Volmer-Weber mechanism. It was established from SEM and EPMA data that lead formed numerous 3D-crystallites with sizes up to 5-8 µm (Fig 4b). In the case of electrochemical co-deposition of these metals, a substantial part of the lead went into the copper thin film and a solid solution formed (Fig 4c). In the case of copper deposition and co-deposition with lead, the CuK\textsubscript{α} intensity is high and constant according to TXRF data (compare Figs 4a and 4c). At the same time the PbL\textsubscript{α} intensity is at the noise level in TXRF spectrum under lead deposition, although the quantities of the deposited copper and lead were comparable (Fig 4b) as estimated using EPMA data [10]. In the case of the electrochemical metal co-deposition, the PbL\textsubscript{α} intensity increased by more than 600 times (compare Figs 4b and 4c). The other fluorescence lines in TXRF spectrum belonged to some trace elements (Ag, Pt, etc.) on the plane areas of the GCC electrode surface uncovered by the lead phase (Fig 4b). Silver was a component of the reference electrode material. Platinum was a material of the counter electrode of the electrochemical cell used.

**CONCLUSIONS**

In this work we have formulated the some basic principles of the direct theoretical description of the influence of heterogeneous surface morphology on analytical signal (X-ray fluorescence line) formation during TXRF measurements. It was demonstrated that TXRF could be effectively applied for identification of mechanisms of nucleation and growth of metal and alloy electrodeposits on foreign low-density substrate. The experimental examples considered emphasize the necessity to account for surface morphology during conventional analytical TXRF procedures.

**REFERENCES**


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