



HAL
open science

THIN FILM COMPOSITIONAL ANALYSIS BY LOW-ENERGY ELECTRON-INDUCED X-RAY SPECTROMETRY (LEEIXS). NEW APPLICATIONS

M. Romand, M. Charbonnier, F. Gaillard

► **To cite this version:**

M. Romand, M. Charbonnier, F. Gaillard. THIN FILM COMPOSITIONAL ANALYSIS BY LOW-ENERGY ELECTRON-INDUCED X-RAY SPECTROMETRY (LEEIXS). NEW APPLICATIONS. Journal de Physique Colloques, 1987, 48 (C9), pp.C9-87-C9-90. 10.1051/jphyscol:1987912 . jpa-00227228

HAL Id: jpa-00227228

<https://hal.science/jpa-00227228>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

THIN FILM COMPOSITIONAL ANALYSIS BY LOW-ENERGY ELECTRON-INDUCED X-RAY SPECTROMETRY (LEEIXS). NEW APPLICATIONS

M. ROMAND, M. CHARBONNIER and F. GAILLARD

Département de Chimie Appliquée et Génie Chimique (CNRS UA-417), Université Claude Bernard Lyon-I, F-69622 Villeurbanne Cedex, France

Résumé - Les possibilités de la spectrométrie d'émission x induite par excitation électronique de basse énergie (LEEIXS) en tant que technique d'analyse des films ultra-minces et des éléments légers sont mises en évidence. Les situations analytiques en LEEIXS et en microsonde électronique (EMP) sont comparées. Une discussion des concepts physiques est incluse en vue de fournir une base pour interpréter les résultats des études présentes et futures.

Abstract - Capabilities of low-energy electron-induced x-ray spectrometry for very thin film and light element analysis are illustrated. The analytical situations in LEEIXS and electron microprobe (EMP) are compared. A discussion of the physical concepts is included in order to provide a basis for interpretation of the results of present and futur investigations.

In the field of material characterization, interest has considerably shifted over the last 15 years from bulk to surface and to thin films problems. One of the main consequences of this increasing demand has been the development of a variety of new spectroscopic techniques with different sensitivity, lateral and depth resolutions.. In this general context, it is the purpose of this paper to show that exciting progress in quantitative analysis of thin films and surface layers can be performed using low-energy electron-induced x-ray spectrometry (LEEIXS) and that this technique is particularly well-suited for investigations in the soft and ultra-soft x-ray range.

I - EXPERIMENTAL

The details of this technique have been recently described /1/ and then only a brief description is given here. The instrument is a wavelength-dispersive x-ray spectrometer. The main feature of this equipment is the use of a gas discharge tube operating as the source of electrons under the primary vacuum of the spectrometer. The energy of the electron beam bombarding the sample surface is selectable over the range 0.5 to 5 keV with currents chosen between 0.1 and 1 mA. Typically the probed area is about 1 cm². X-rays are dispersed by using flat crystals (or pseudo-crystals) and detected by a gas flow-proportional counter.

It should be here noted that the basic process of the characteristic x-ray emission under a primary electron impact is similar in LEEIXS and electron microprobe (EMP) and that EMP differs from LEEIXS essentially in terms of nature of the source, energy of the electron beam (typically 10 to 30 keV) and focusing of this beam into a spot generally 0.1 - 1 μ m in diameter. As a consequence of the energies used in EMP typical sampling depths range from 0.2 to 1 μ m i.e. to values largely higher than those analyzed in LEEIXS (commonly some tens of nm).

II - THEORY

If the determination of composition and thickness of thin films is one of the classical fields of electron probe microanalysis (EPMA), almost all the studied

systems are coating-substrat combinations in which the analyzed element of the coating is not present in the substrat and is not of low atomic number (i.e. elements such as B, C, O, ...). This last limitation is due to the very small intensities measured for the characteristic x-ray lines of these elements. This experimental fact results partly from the low fluorescence yield (e.g. $\omega_K = 0.0085$ for oxygen) and therefore from the relatively low x-ray production cross-section $\sigma_K = \sigma_K \omega_K$, the corresponding ionization cross-section σ_K for the K shell being approximately $5 \cdot 10^{-20} \text{ cm}^2$ for oxygen and 15 keV electrons, but also partly from the relatively small number of atoms giving the information within the sampled volume (about 10^{-12} cm^3 in the general case). Figure 1 compares the situations in EMP and LEEIXS. In the case of EMP it is represented a typical x-ray emitting pear-shaped volume and the escape depth (200 - 300 nm) of soft x-rays when significant absorption effects occur within the excited target. On the contrary LEEIXS is commonly capable of analyzing a volume of material about $100 \text{ nm} \times 1 \text{ cm}^2 = 10^{-5} \text{ cm}^3$ i.e. a volume about 10^7 times greater than the one giving the information in EMP. These simple considerations explain the potential of LEEIXS in long wavelength x-ray emission even though fluorescence yields are low, ionization cross-sections are only slightly higher (about $1 \cdot 10^{-19} \text{ cm}^3$ for oxygen and 1-2 keV electrons) than those corresponding to higher energies in EMP, and other parameters such as beam current and spectrometer efficiency are less favourable.

As in the case of EMP, the use of LEEIXS for practical purposes needs to gain a better knowledge of the x-ray generation depth in the specimen. Figure 2 shows, as a function of the incident electron beam energy E_0 , the generation ranges of OK_α in an iron oxide matrix. Such curves are obtained from various equations which, except Feldman's one [2], are - or have been - largely used in EPMA [3-6]. As can be seen from Figure 2, the choice of an appropriate relation is quite critical in order to estimate the actual sampling depth. Nevertheless and until now, the excitation range R_e as calculated from Feldman's equation has been used in all our LEEIXS investigations. Its main advantage over the other ones is to have been derived from experiments for 1 to 10 keV electrons.

As for EPMA, quantitative analysis by LEEIXS can be carried out by measuring the intensity $I(h\nu_i)$ of an x-ray signal characteristic of an element i . In the general case for which the volume density $N_i(z)$ - in $\text{atoms} \cdot \text{cm}^{-3}$ of the element of interest is only function of the distance z from the surface, $I(h\nu_i)$ can be written in the form :

$$I(h\nu_i) = k \int_{z=0}^{z=R_e} J(z) \cdot N_i(z) \cdot \sigma_i \left[E(z), E_x \right] \cdot \left\{ 1 + \eta \left[E(z), E_x \right] \right\} \cdot \exp \left(-\mu z / \sin \beta \right) dz \quad (1)$$

where k is a constant, $J(z)$ the electron flux at depth z , σ_i the ionization cross-section of the shell x for electrons of energy $E(z)$, η and $\exp \left(-\mu z / \sin \beta \right)$ correction factors which account respectively for the additional ionizations of atoms i by backscattered electrons and for absorption of photons $h\nu_i$ leaving the sample at a mean emergence angle β . It should be noted that the secondary fluorescence excited by the Bremsstrahlung is here neglected. Such a simplified approach may be considered as a rule in the energy range used in LEEIXS and is all the more valid as the mean atomic number of the excited layer is lower. As to the secondary fluorescence excited by characteristic radiations, this possibility corresponds to particular cases and then it has not been taken into account. It should be also noted that, in practice, it is quite difficult to predict by calculation both the absolute generated and measured intensities. Indeed, the variations vs. z or $E(z)$ of several parameters play a very significant role. The case of R_e i.e. the range over which the integration is made has been already discussed. Moreover, it is known that σ is a function of overvoltage E/E_x and is changing rapidly in the low overvoltage range which is used in LEEIXS and that mass absorption coefficients μ for light elements are available with quite large uncertainties.

Obviously Eq. 1 can take simpler forms when special analytical cases are considered. So, for very thin films of thickness $t \ll R_e$ a reasonable assumption can be made that primary electrons suffer no significant energy and flux loss over the depth t and that absorption of x-rays is negligible. Under these conditions :

$$I(h\nu_i) = K \int_0^t N_i(z) dz \quad (2) \quad \text{where } K = k (1 + \eta) J(0) \sigma_i [E_0, E_x]$$

$I(h\nu_i)$ is then proportional to the number of atoms i per unit area (expressed in atoms.cm^{-2}), or to the mass of atoms i per unit area (expressed in units like $\mu\text{g.cm}^{-2}$). For very thin films of homogeneous composition and density $N_i(z) = N_i(0)$, from which $I(h\nu_i) = K N_i(0) t$, t being expressed for instance in nm. In these two cases, absolute quantities may be obtained by comparison to reference standards and in the former case, the results are independent of the shape of the distribution profile $N_i(z)$. The main problem is now to estimate, for a given system, the range of validity of such approximations.

RESULTS AND DISCUSSION

Figure 3 shows LEEIXS spectra of a stainless steel substrate before and after an anodizing in a hot sulfuric acid-potassium dichromate electrolyte. Spectrum (a) is characteristic of the metallic surface after degreasing, chemical pickling and rinsing. The intensity of the OK_{α} emission band is associated with a residual oxide, the thickness of which is about 4 nm. Comparison with spectrum (b) clearly indicates that a relatively "thick" oxide film has grown during anodizing and that such a treatment is responsible for significant changes in the surface concentration of the alloying elements. The case of chromium is here obvious.

Figure 4 is concerned with thermal oxide films formed on stainless steel substrates at 600°C . It shows for two different values of E_0 the variations of the OK_{α} intensity as a function of film thickness. The two corresponding curves are normalized at a same maximal intensity. More particularly it can be noted :

(i) that exists in each case a finite thickness range for which there is a linear relationship between OK_{α} intensity and oxide film thickness. The extent of this linear zone increases with E_0 . Comparison of curve (b) with data extracted from Fig. 2 for an energy of 2 keV leads to the observation that the extent of this linear zone is reduced to about one half of the value of the x-ray generation range R_e calculated for a bulk sample of same composition ;

(ii) that exists (for curve (b)) an asymptotic part which is associated with oxide film thicknesses greater than R_e . Such films can be considered as being of infinite thickness for the used value of E_0 (2 keV in the present case) ;

(iii) that exists lastly a range of intermediate thicknesses for which, among other things, electron energy loss and/or absorption attenuation cannot be assumed as negligible. In this case, standards of nearly the same composition as the specimen should be used in order to perform accurate analyses. Obviously another possibility consists of carrying out experiments with a higher value of E_0 i.e. consists of increasing the extent of the linear zone (see curve (a)).

In dealing with this special example it is clearly seen that for any metal/oxide system it is possible to know experimentally for what thickness and electron beam energy E_0 some corrections have or have not to be done.

CONCLUSIONS

The practical examples presented here demonstrate that capabilities of the soft x-ray spectrometry for characterizing surface and near-surface of solid materials have until now been largely under-estimated. In this context it is easy to expect the futur development of LEEIXS which probes surface layers and very thin films in non-UHV conditions and which extends the possibilities and application fields of surface spectroscopic analyses. Obviously, works dealing with new practical systems are presently in progress in order to test the reliability of the approaches discussed in this paper.

REFERENCES

1. ROMAND M., BADOR R., CHARBONNIER M. and GAILLARD F., X-ray Spectrom. 16 (1987) 7
2. FELDMAN C., Phys. Rev., 117 (1960) 455

3. REED S.J.B., Proc. 4th Int. Congr. on x-ray Optics and Microanalysis (Hermann, Paris) (1966) 339
4. ANDERSEN C.A. and HASSLER M.F., *ibid* (1966) 310
5. CASTAING R., Adv. Electronics and Electron Phys., 13 (1960) 317
6. KANAYA K. and OKAYAMA S., J. Phys. D., Appl. Phys. 5 (1972) 43

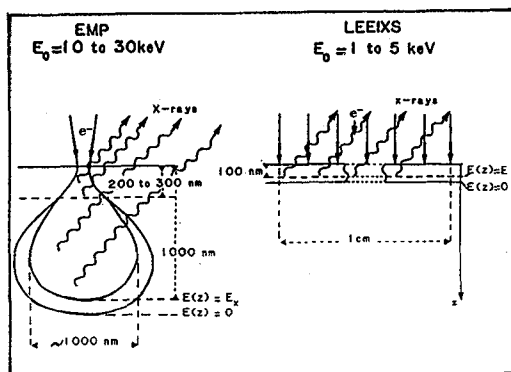


Fig. 1 - Schematic representation of the interaction of an electron beam with a solid surface in EMP and LEEIXS.

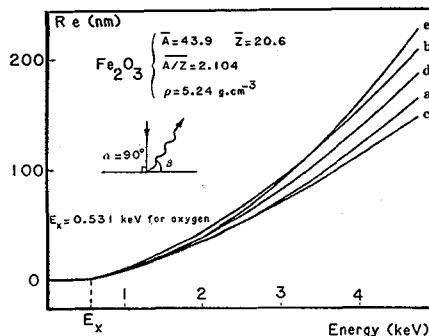


Fig. 2 - Calculated OK_{α} excitation thickness vs. incident electron beam energy for the equations due to : a /4/, b /6/, c /3/, d /5/, e /2/.

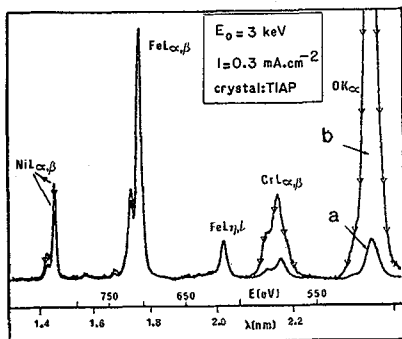


Fig. 3 - LEEIXS spectra of a stainless steel (304 L) surface before (a) and after (b) anodizing in a hot $H_2SO_4 - K_2Cr_2O_7$ bath.

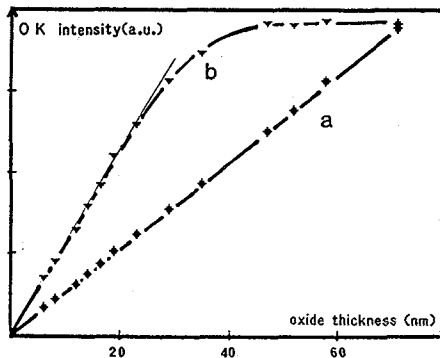


Fig. 4 - Intensity variation of OK_{α} as a function of oxide film thickness for thermally oxidized stainless steel (316 L) substrates and for $E_0 = 2$ keV (b), and 4.5 keV (a). Calibration of film thickness is made by RBS (Rutherford Backscattering Spectrometry).