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

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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 future 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 µm in diameter. As a consequence of the energies used in EMP typical sampling depths range from 0.2 to 1 µm 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. ele-
ments such as B, C, O, ...). This last limitation is due to the very small intensi-
ties measured for the characteristic x-ray lines of these elements. This experimen-
tal 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
\( \sigma_x = \sigma_K \omega_K \), the corresponding ionization cross-section \( \sigma_K \) for the K shell being
approximately \( 5.10^{-20} \) 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 absorp-
tion effects occur within the excited target. On the contrary LEEIXS is commonly capable
of analyzing a volume of material about 100 nm x 1 cm\(^2\) = \( 10^{-5} \) cm\(^3\) i.e. a volume about
10\(^7\) times greater than the one giving the information in EMP. These simple considera-
tions 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 \( 1.10^{-19} \) 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\(_x\) in an
iron oxide matrix. Such curves are obtained from various equations, 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 investiga-
tions. 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 atoms.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:

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

where \( k \) is a constant, \( J(z) \) the electron flux at depth \( z \), \( \sigma_i \) the ionization cross-
section of the shell \( x \) for electrons of energy \( E(z) \), \( \eta \) and \( \exp \left[ -\mu vz / \sin \beta \right] \) - 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 \( \beta \). 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 integra-
tion is made has been already discussed. Moreover, it is known that \( \sigma \) 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 \( \mu \) 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:

\[
\text{...}
\]
\[ I(h\nu_i) = K \int_0^t N_i(z) \, dz \] (2) where \( K = k (I + q) J(0) \sigma_i \left[ E_0, Ex \right] \)

\( I(h\nu_i) \) 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 \( \mu g.cm^{-2} \)). 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\(_\alpha\) 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\(_\alpha\) 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\(_\alpha\) 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 \( R_0 \) 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 \( R_0 \). 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

2. FELDMAN C., Phys. Rev., 117 (1960) 455
4. ANDERSEN C.A. and HASSLER M.F., ibid (1966) 310

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

Fig. 2 - Calculated OKβ 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 H2SO4 - K2Cr2O7 bath.

Fig. 4 - Intensity variation of OKβ as a function of oxide film thickness for thermally oxidized stainless steel (316 L) substrates and for E₀ = 2 keV (b), and 4.5 keV (a). Calibration of film thickness is made by RBS (Rutherford Backscattering Spectrometry).