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## LOW-ENERGY ELECTRON-INDUCED X-RAY SPECTROMETRY : A TECHNIQUE FOR SOLID SURFACE STUDIES

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**Résumé** - Ce travail décrit des applications nouvelles de la spectrométrie LEEIXS en tant qu'outil d'analyse et de caractérisation des surfaces solides (de quelques dizaines à quelques centaines d'Å d'épaisseur). Les exemples présentés mettent en évidence des ségrégations élémentaires à la surface de substrats métalliques (alliages de titane ou d'aluminium) soumis à différents traitements chimiques ou électrochimiques. Par ailleurs, on montre comment des informations sur l'état chimique des éléments peuvent être extraites de la structure des bandes d'émission X. Le procédé consiste à utiliser les spectres dérivés après un filtrage par transformée de Fourier des courbes expérimentales. Les exemples présentés concernent la bande d'émission K de l'oxygène caractéristique de différents verres, des oxydes d'étain et des oxydes de titane.

**Abstract** - New capabilities of low-energy electron-induced x-ray spectrometry (LEEIXS) for providing chemical information about the first hundreds Å of a solid surface are described. Examples are concerned with the surface segregation of impurities or alloying elements when titanium or aluminium alloys are subjected to chemical or electrochemical treatments. In addition, it is shown how chemical state information contained in x-ray emission bands may be enhanced by using derivative spectra after a Fourier transform filtering of the experimental curves. Examples dealing with the oxygen K emission band of different glasses, tin or titanium oxides are given.

When an electron beam interacts with a solid, inner-shell vacancies may be produced. Atoms in an excitation state return to a state nearer the ground one by the decay of upper shell electrons into core holes. The excess energy associated with such a transition either is transferred to another electron which is ejected as an Auger electron or is released as a characteristic x-ray photon. When some keV primary electrons are used these two relaxation processes are the basic principles of two material characterization methods : Soft x-ray Spectrometry (SXS) and Auger Electron Spectrometry (AES). AES is one of the most powerful surface sensitive techniques available to-day, but the capabilities of SXS in this field are largely under-exploited. The main purpose of the present work is to show that progress in surface analysis can also be performed by using low-energy electron-induced x-ray Spectrometry (LEEIXS).

The details of this technique have been described previously /1,2/ ; hence, only a brief description is given here. The instrument is a wavelength-dispersive x-ray spectrometer equipped with a cold cathode tube. This gas tube is an electronic excitation source running in the primary vacuum of the spectrometer. The electron beam energy is selected in the range 0.5-5 keV ; the current density is chosen less than 1 mA.cm<sup>-2</sup>. In LEEIXS, typical emission depths range from 50 to 1000 Å. This parameter is determined mainly by the energy attenuation of the in-going primary electrons and also depends on the target material nature.

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First examples of LEEIXS applications are given in order to emphasize how chemical or electrochemical treatments of metallic substrates change the surface composition by modifying alloying element concentrations.

Figure 1 shows  $\text{SnL}_{\alpha,\beta}$  spectra recorded from titanium alloys Ti-5Al-2.5Sn subjected to various surface chemical treatments. Treatment (a) is simply a degreasing step which strips the "as received" alloy of major surface contaminants, treatments (b), (c) and (d) are respectively fluoro-nitric, fluoro-phosphate and fluoro-ammonium etchings. The  $\text{SnL}_{\alpha,\beta}$  spectrum (e) of a Sn substrate only recovered with its natural oxide layer is shown for comparison purpose. From these spectrometric data, it clearly appears that different chemical treatments of the investigated alloy produce significant differences in surface composition. More particularly it may be noticed that the fluoro-ammonium etch leaves the surface very rich in Sn. Complementary results put forward that the main effect of this treatment is to produce a surface covered with a thin layer of tin oxide  $\text{SnO}_2$  /1/ while the oxide layer is found to be mainly  $\text{TiO}_2$  when treatments (b) and (c) are used.

Figure 2 is concerned with Ga impurities which are incorporated into an anodic aluminium oxide grown on an aluminium substrate. Spectra (a) and (b) represent  $\text{GaL}_{2,3}$  emission lines of the investigated material respectively prior and after an anodization in a phosphoric bath. Comparison between these two spectra clearly indicates a significant Ga impurity segregation from the metallic substrate toward the oxide film during the anodizing process.

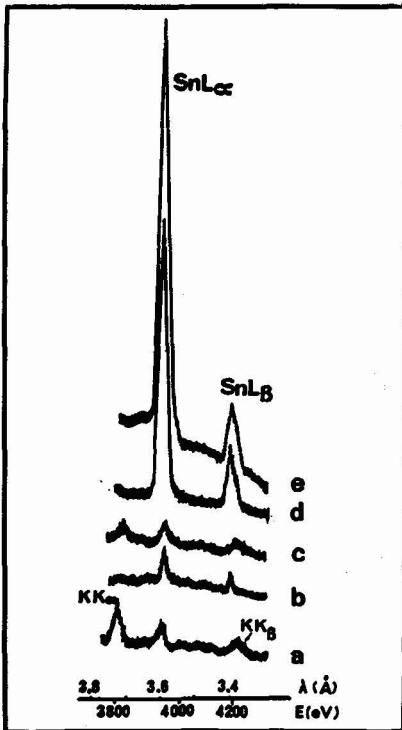


Fig. 1 -  $\text{SnL}_{\alpha,\beta}$  emission spectra dispersed by a Ge crystal ( $2d = 6.532 \text{ \AA}$ ). Electron beam energy : 4.5 keV ; probed depth : 500  $\text{\AA}$  or so ; current density : 0.5  $\text{mA}\cdot\text{cm}^{-2}$  ;

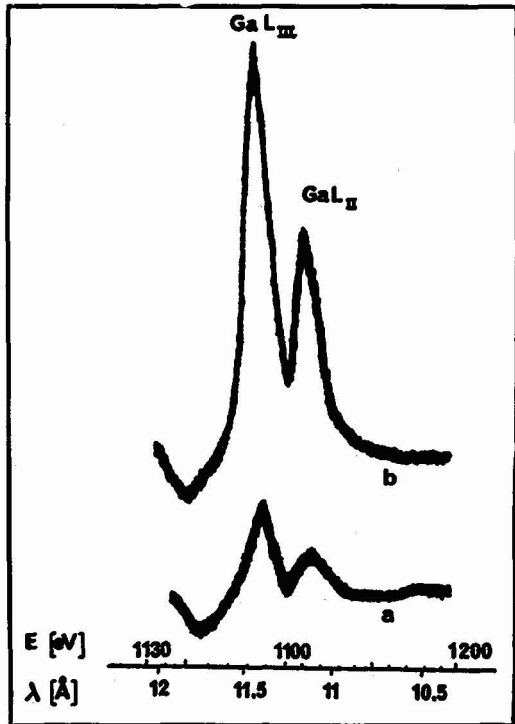


Fig. 2 -  $\text{GaL}_{2,3}$  emission spectra dispersed by a TlAP crystal ( $2d = 25.90 \text{ \AA}$ ). Electron beam energy : 3 keV ; probed depth : 1100  $\text{\AA}$  or so ; current density : 0.5  $\text{mA}\cdot\text{cm}^{-2}$

In addition, it is shown that information on the chemical state of an element can be obtained from the fine features (line shape, energy shift) of some x-ray emission bands and that significant improvements can be achieved by using derivative spectra after Fourier Transform (FT) filtering /3/.

By way of example, Figure 3 shows oxygen K emission bands of borosilicate (a) and soda-lime silicate (b) glasses. Experimental spectra  $N(E)$  are directly obtained by intensity measurements at 1024 angular positions during a 5 minutes continuous wavelength scanning over  $5^\circ \theta$ . After a direct FT operation, the high frequency domain relating to random experimental noise is easily removed by multiplying the FT by a filtering function (Hanning filter) with an appropriate cut-off frequency. Then, reciprocal FT calculations provide the smoothed direct spectra. Owing to this procedure, accurate derivative spectra  $dN(E)/dE$  can be obtained and a greater information recovery can be achieved. In the present case, the two different glasses can be easily distinguished by considering, on the derivative curves, the peak-to-peak ratio (A/B) corresponding to the main and the low-energy OK sub-bands. This parameter is equal to 6.7 and 12.9 in cases (a) and (b), respectively.

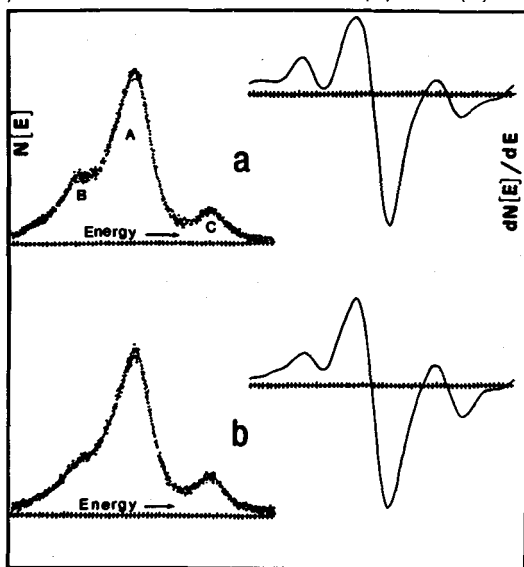


Fig. 3 - Direct and derivative OK emission spectra for borosilicate (a) and soda-lime silicate (b) glasses. Electron beam energy : 1.5 keV ; current density :  $0.5 \text{ mA.cm}^{-2}$ . Direct spectra are dispersed with a RbAP crystal ( $2d = 26.12 \text{ \AA}$ ). The high energy sub-band C is mainly due to a line-like reflectivity structure that phthalate acid analyzing crystals exhibit at about 531 eV.

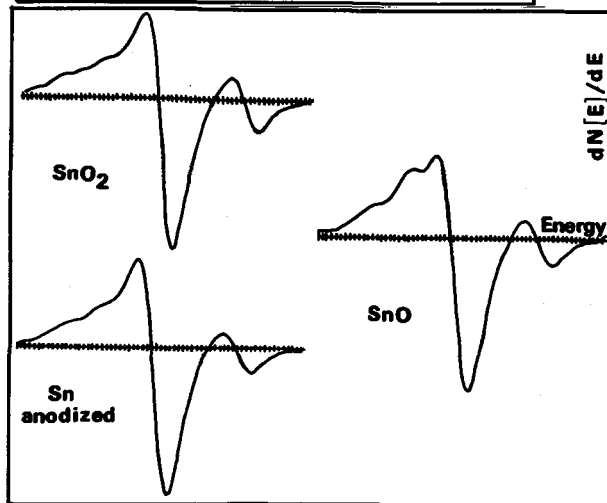


Fig. 4 - Derivative OK emission spectra for tin oxides  $\text{SnO}_2$  and  $\text{SnO}$  and for an anodic oxide grown on a Sn substrate.

In a similar way, Figure 4 shows derivative OK emission spectra from  $\text{SnO}_2$  and  $\text{SnO}$  oxides and from a tin substrate anodized in a tartaric acid electrolyte. The chemical composition of the anodized specimen can be unambiguously identified as  $\text{SnO}_2$ . Note that an analogous conclusion has been previously drawn comparing in a simpler way the full width at half maximum of the relevant overall OK bands /1/.

Lastly, Figure 5 represents derivative OK emission spectra from  $\text{TiO}_2$  and  $\text{TiO}$  oxides and from a titanium substrate anodized in a tartaric acid electrolyte in a way which produces an outer oxide layer  $\text{TiO}_2$ -like and an inner oxide layer  $\text{TiO}$ -like /4/. These last spectra have been performed with various electron beam energies in order to probe greater and greater oxide thicknesses. The observed spectral changes concerning mainly low-energy components are thought to be related to the stoichiometry variations when thicker materials are probed. Such results offer convincing evidence that work has to be pursued in that direction for deducing chemical bonding changes.

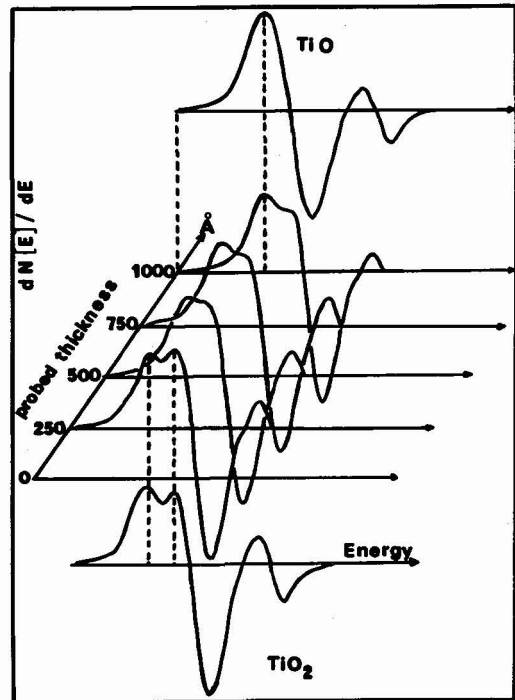


Fig. 5 - Derivative OK emission spectra for titanium oxides  $\text{TiO}_2$  and  $\text{TiO}$  and for an anodic oxide grown on a Ti substrate. Direct intermediary spectra are performed at various electron beam energies in order to probe greater and greater thicknesses.

#### CONCLUSIONS

The above results clearly demonstrate that soft x-ray emission can be used for studying the near-surface chemical composition of solids. More particularly, LEEIXS appears to be a practical tool for investigating various materials which have undergone specific surface processes. In addition, it is emphasized that significant improvements can be achieved in chemical bonding characterization by using derivative spectra obtained after Fourier transform filtering of the experimental x-ray emission bands.

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