

NEW PERFORMANCES OF SOFT X-RAY SPECTROMETRY (LEEIXS) IN SURFACE ANALYSIS OF ORGANIC AND INORGANIC MATERIALS

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ABSTRACT

Capabilities of low-energy electron induced x-ray spectrometry (LEEIXS) in surface and very thin film analysis are illustrated by examples dealing with films of organic and inorganic materials deposited on different metallic substrates from liquid or vapour phases (chemisorption, electrodeposition, plasma polymerization ...). In addition, these examples point out the sensitivity of the technique down to the submonolayer range and highlight the potential of LEEIXS as a well-suited optimisation and monitoring tool for surface treatment processes.

INTRODUCTION

Within the last two decades, analysis and characterization of surfaces, interfaces and very thin films have become of considerable importance in many fields of pure and applied research and of modern technological developments. Indeed, it should be highlighted that today, surface modifications and thin film deposition processes are commonly used for a variety of purposes in microelectronics, engineering, optical, aerospace, biomedical, and other applications and that there exists many requirements for establishing reliable relations between the formation parameters and characteristic properties of thin films and the composition and structure of these latter, in particular at and near the interfacial zones of multi-component structures. Under these conditions, it is easy to understand why an increasingly higher demand has led to a rapid development of various surface and near-surface analytical techniques. Some of these methods such as x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS) and ion scattering spectroscopy (ISS) have matured both with respect to instrumentation and methodology and therefore are now well-established. However, many others are yet in their infancy even though they possess a large potential. Typically, this is the case of low-energy electron induced x-ray spectrometry (LEEIXS) [1-3], whose worldwide extension remains relatively limited because the leading laboratories in Surface Science think primarily in terms of techniques operating in an ultra-high vacuum (UHV) environment and furthermore are not well disposed to works requiring the dispersion and detection of soft and ultra-soft x-rays.

The main purpose of the present work consists first of recalling briefly the basic principles of LEEIXS and second of reporting some new applications which illustrate the various capabilities of this technique as a characterization tool for thin and ultra-thin films, whatever be their conducting or insulating nature, as well as an optimization and monitoring tool for surface treatment processes.

EXPERIMENTAL

The LEEIXS instrument is basically a wavelength-dispersive X-ray spectrometer in which the excitation tube is an electronically-stabilized gas-discharge source. Such a system works as an

electron source operating under the primary vacuum of the spectrometer. The quasi-monokinetic electron beam generated is not focused on the sample surface as is the case in an electron microanalyser (EPMA) and the area analyzed is less than 1 cm^2 . The latter depends on the choice of the size of the circular aperture of the anode which allows a part of the electron beam to escape from the discharge tube and to reach the specimen under investigation. Typically, the energy of the incident electron beam is selected between 1 and 5 keV with a current between 0.1 and 0.3 mA. Soft and ultrasoft X-rays emitted in such conditions are dispersed as a function of their wavelength by suitable flat analyzing crystals, pseudo-crystals or synthetic multilayers and detected by a flow-proportional detector equipped with a thin aluminized polypropylene window ($0.5 \text{ }\mu\text{m}$) and swept with a conventional 90 % Ar - 10 % CH₄ gas mixture. The depth probed depends, among other parameters, on the incident electron beam energy and on the chemical nature of the sample and typically ranges from 50 to 100 nm. This technique allows both atomic (qualitative and quantitative) and molecular (qualitative) analysis. It should be noted that LEEIXS is particularly well suited to light element detection (B, C, N, O, F, ... from their K α radiations) owing to a high ionization cross-section of the K shells by low-energy electrons and a relatively high current of the incident electron beam penetrating in a relatively large sample volume ($\sim 10^{-5} \text{ cm}^3$) in comparison with the corresponding volume probed in EPMA ($\sim 10^{-12} \text{ cm}^3$). In addition, it should also be said that LEEIXS, considering the excitation source used, allows the analysis of insulating samples without the need to cover them with a conducting film, and that the current density of the electron beam at the sample surface is normally chosen low enough (*e.g.*, 0.1 mA.cm^{-2}) to prevent the degradation of many materials and more particularly of various organic ones [4].

RESULTS AND DISCUSSION

In dealing with the sensitivity of LEEIXS for light elements, it was shown in a previous paper [3] that the minimum mass of oxide detectable on the surface of a stainless steel substrate would correspond theoretically to a surface coverage lower than a tenth of monolayer ($\sim 10^{-2} \text{ }\mu\text{g.cm}^{-2}$ of a Cr₂O₃/Fe₂O₃ oxide). Corresponding measurements were carried out via dispersion (Thallium acid phthalate crystal / TIAP) and detection of O K α radiations by using a counting time of 20 s and the conventional 3σ criterion *i.e.* a film thickness which would give an O K α intensity equal to three times the standard deviation of the background at the same wavelength. For the same purpose, there was studied in the present work the chemisorption on gold surfaces of organosulfurized derivatives, *viz.* n-alkyl thiols SH-(CH₂)_n-CH₃ with $n + 1 = 3, 6, 8, 12$ and 16 . Such species are known to coordinate strongly to gold as self-assembled monolayers with the probable formation of thiolates RS-Au (I) [5]. The substrates covered with ordered organic monolayers were directly investigated by LEEIXS. Figure 1 represents the C K α spectrum of a chemisorbed monolayer corresponding to $n + 1 = 16$ atoms of carbon. This experiment was carried out using a 3 keV electron beam and a current intensity of 0.1 mA. The C K α radiation was dispersed using an octadecyl hydrogen maleate crystal / OHM ($2d = 6.35 \text{ nm}$) which possesses higher performance over the conventional lead stearate pseudo-crystal ($2d \cong 10 \text{ nm}$) both in terms of reflectivity and spectral resolution. In the present example, the net intensity of the C K α signal is about 100 cts.s^{-1} . In addition, figure 2 shows the increase of the C K α emission band intensity as a function of the number of carbon atoms in the adsorbed molecule. The change in curve slope for $n + 1 > 12$ is attributable to the fact that thiols form a densely-packed, crystal-

like assembly as chain length increases [5]. As can be seen, the increase in the peak count rate is obvious. This example again demonstrates that LEEIXS is quite able to analyze light elements such as carbon down to the sub-monolayer range. However it is important to point out that backscattering processes are responsible for a part of the total production of the C K α radiations. Indeed, it should be recalled that the backscattering coefficient increases with increasing atomic number of the target and therefore, in the present case, that the reemergent beam of electrons backscattered by the gold substrate causes additional ionizations of the K level of carbon atoms which are present in the organic surface layer. It should also be mentioned that the same phenomena are commonly encountered in AES. Indeed, the intensity of an Auger peak involves a backscattering factor depending on the material in which backscattering takes place.

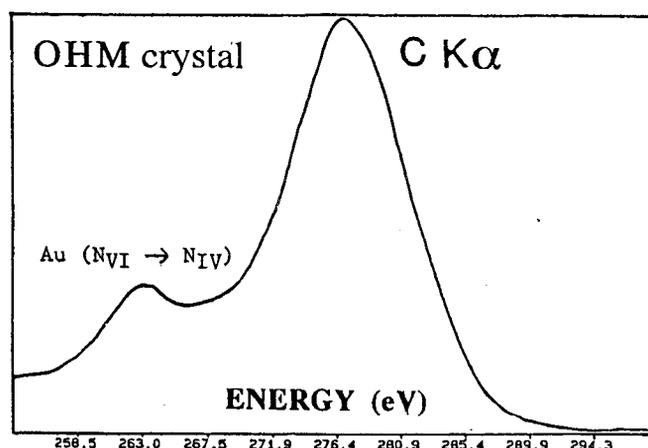


Fig. 1: C K α spectrum of an alkanethiol (C 16) chemisorbed as self-assembled monolayers (SAM) on a gold surface.

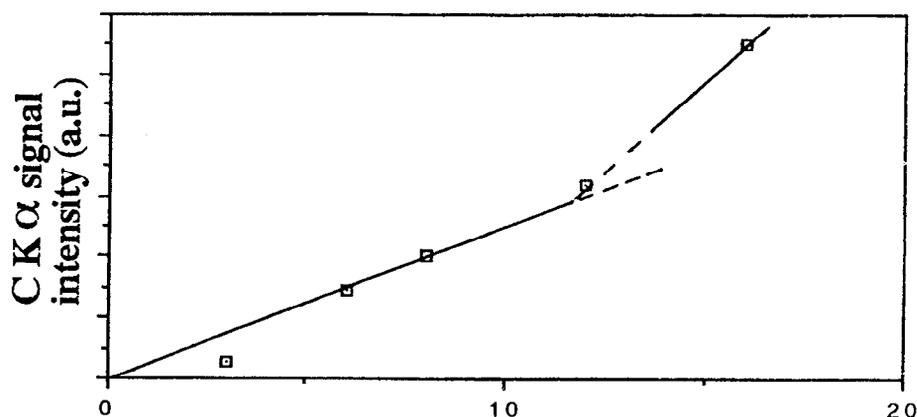


Fig. 2: Intensity variation of the C K α emission band of alkanethiols chemisorbed (as SAM) on a gold surface, as a function of the chain-length (number of carbon atoms).

The next examples deal with the characterization of organic/inorganic material films deposited on metallic substrates. In a first step consider the formation of films produced by a glow-discharge process (plasma-enhanced chemical vapor deposition / PACVD) onto stainless steel substrates. It should be recalled that such a process permits depositing thin films from a

the probed depth providing the C $K\alpha$ information can be evaluated at about 200 nm. This value is obtained using one of the x-ray generation range (Feldman's equation for instance) (see ref. [2]) and assuming a density of the film material equals to 1.9. In addition it should be said that thickness calibration was also performed by gravimetry for thicker films, and assumed that the relationship between deposition time and mass thickness is valid in the low thickness range. Furthermore, figure 3 represents the intensity variation of the Fe $L_{\alpha,\beta}$ emission band which is characteristic of a signal emitted by the stainless steel substrate. In this case, the corresponding Fe $L_{\alpha,\beta}$ radiation was dispersed using a TiAP crystal ($2d = 2.574$ nm). Obviously, the Fe $L_{\alpha,\beta}$ signal intensity decreases as film thickness increases.

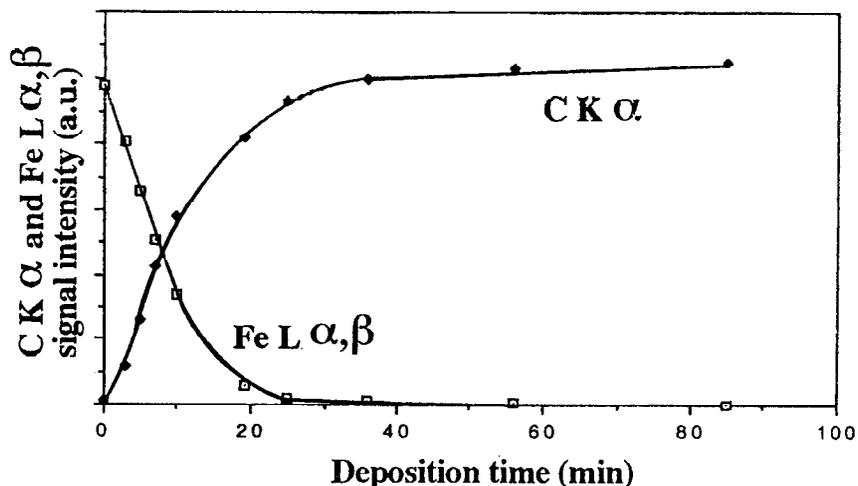


Fig. 3: Intensity variation of the C $K\alpha$ and Fe $L_{\alpha,\beta}$ emission bands of a-C:H films deposited on stainless steel substrates by a PACVD process, as a function of deposition time.

The main objective of the research developed in our laboratory concerning the deposit of very thin a-C:H films on metallic substrates was to demonstrate that such films could play a dual role of anti-corrosion barrier and adhesion "primer" [6]. However, because of their chemical inertness, the hydrogenated carbon films have no natural tendency to establish strong chemical bonds with adhesive, paint, varnish-like organic coatings. For improving such a situation, the film surface has firstly to be made chemically active *e.g.* via plasma functionalization. Unfortunately, during plasma treatment there exists competition between surface functionalization and surface etching. As it is well known, the effects of surface functionalization can easily be investigated by XPS. On the other hand, the effects of surface etching which leads to change in film thickness can be controlled by LEEIXS. Such investigations were carried out by following the intensity variation of the C $K\alpha$ radiation emitted by the film and the Fe $L_{\alpha,\beta}$ radiation emitted by the substrate as a function of plasma duration. All these experiments were performed on films of same initial thickness (about 80 nm) by changing the nature of the etching gas while all other etching parameters (gas pressure and flow rate, rf power) were held fixed. Figure 4 shows, as etching progresses, the C $K\alpha$ intensity decreasing and the corresponding Fe $L_{\alpha,\beta}$ intensity increasing, for He, Ar, NH_3 , O_2 plasma, respectively. As can be seen, the O_2 plasma is responsible for a much stronger etching than other plasmas. Indeed, in addition to a mechanical effect due to the ion bombardement of the target, a pronounced chemical effect occurs in this case since oxygenated

species produced within the plasma react with the carbon film and give CO, CO₂ and H₂O volatile molecules which are evacuated by the pumping system.

In the same way as a-C:H films were obtained from a pure CH₄ vapour phase by a PACVD process, plasma polymerized siloxane films were deposited onto stainless steel substrates. Prior to plasma polymerization, the substrates were subjected to an oxygen plasma treatment to remove surface contaminants. In the present experiments, tetraethoxysilane (TEOS) was used as a precursor liquid and TEOS vapour was made available in the reactor by decreasing

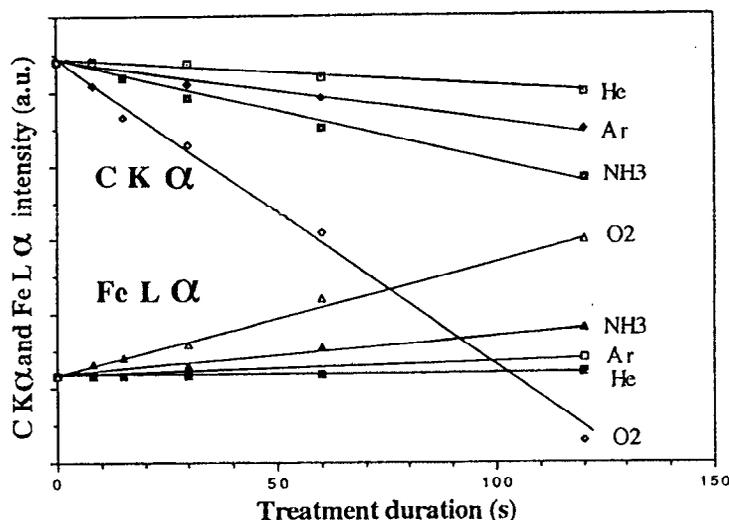


Fig. 4: Intensity variation of the C K α and Fe L α,β emission bands of an a-C:H film (80 nm in thickness) deposited on a stainless steel substrate, as a function of He, Ar, NH₃ and O₂ plasma duration.

the pressure above the liquid phase which is contained in an additional vessel or by using argon as a carrier gas. As example, figure 5 represents the intensity variation of the Si K α , O K α , C K α and Fe L α,β emission line or bands as a function of the deposition time. In the present case, LEEIXS analyses were carried out by changing the energy of the incident electron beam between 3.3 and 2.7 keV so that the material thickness providing the analytical information was always the same (about 10 nm) whatever be the radiation detected. As can be seen, for a deposition time corresponding to this thickness, the intensity of the Fe L α,β signal emitted by the substrate cancels out.

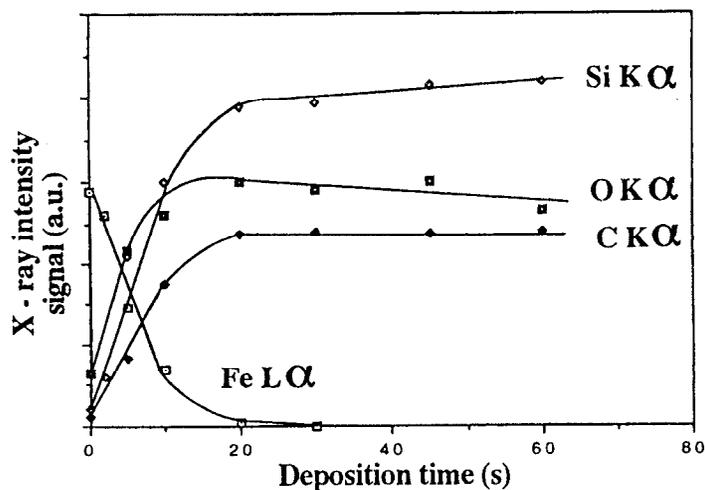


Fig. 5: Intensity variation of the Si K α , O K α , C K α and Fe L α,β emission line or bands of siloxane films deposited on stainless steel substrates by a PACVD process, as a function of deposition time.

The next examples are concerned with polymer films produced this time from a liquid phase. The first one deals with the electrodeposition of a γ -aminopropyltriethoxysilane (γ -APS) on aluminium substrates. In this work the samples were immersed in an hydroalcoholic silane solution whose the natural pH (10.6) was lowered by adding hydrochloric acid. The cathodic deposition was obtained by passing a current through the solution, under a constant applied voltage between Al and Pt electrodes. After deposition, the substrates were rinsed in order to remove loosely bound species. In a first step, the change of the amount of the electrodeposited coating was followed using LEEIXS. Figure 6 gives results concerning the influence of deposition time on the Si K α and Al K α signal intensities for films obtained at 10 volts and with a solution at pH = 9.2. In these experiments, a 4 keV electron beam and a current intensity of 0.1 mA were used. Al K α and Si K α radiations were dispersed using a PET crystal ($2d = 0.875$ nm). In agreement with the expectation the intensity of the Al K α radiation emitted by the substrate decreases and the intensity of the Si K α radiation emitted by the polymer film increases which is a direct proof that a polymer cation adsorption has taken place on the metal surface during the electrochemical process. In a second step, figure 7 shows the effects observed when varying both the voltage between 3 and 10 volts and the pH (2.5 ; 8.7 and 9.2 respectively) for a constant deposition time of 15 min. It should be noted that in each case the corresponding curves reach nearly a plateau which indicates the formation of a polymer film less and less conductive limiting thus its growth to a maximum thickness clearly less than 10 nm as that may be confirmed by XPS measurements [7].

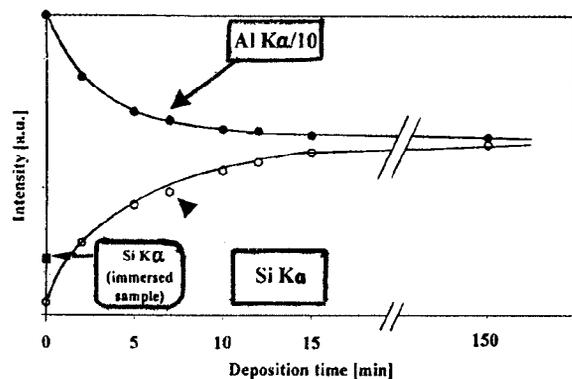


Fig. 6: Intensity variation of the Si K α and Al K α emission lines of electrodeposited-silane films on aluminium substrates, as a function of deposition time. The Si K α intensity for a sample only immersed in the silane solution is also shown.

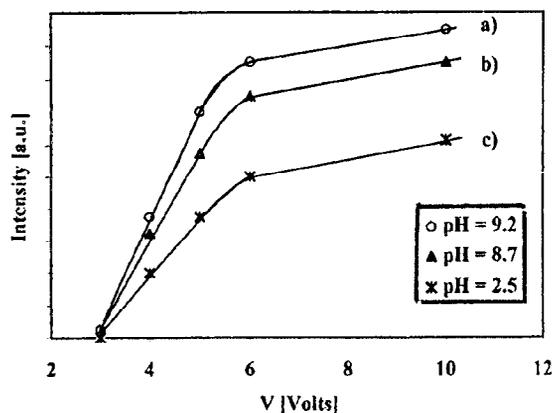


Fig. 7: Intensity variation of the Si K α emission line of electrodeposited-silane films on aluminium substrates, as a function of the substrate-Pt anode voltage and pH of the silane solution.

In a similar way, figure 8 is relative to the chemisorption of a γ -glycidoxypropyltrimethylsilane (γ -GPS) on stainless steel substrates from an hydroalcoholic silane solution. The silane films obtained were dried under a stream of nitrogen, heated in air then rinsed in distilled water in order to remove any weakly bound or physisorbed species. Figure 8 provides LEEIXS results and shows the C K α , O K α and Si K α band or line intensity variations as a function of the γ -GPS concentration in the solution. In these experiments, the energy of the incident electron beam was 3 (C and O analysis) and 4.5 keV (Si analysis), respectively and the current intensity was 0.1 mA. C K α , O K α and Si K α radiations were dispersed using OHM, TIAP and PET crystals, respectively. As can be seen, the silane film thickness which is here directly proportional to the Si K α intensity increases until a γ -GPS concentration in the solution

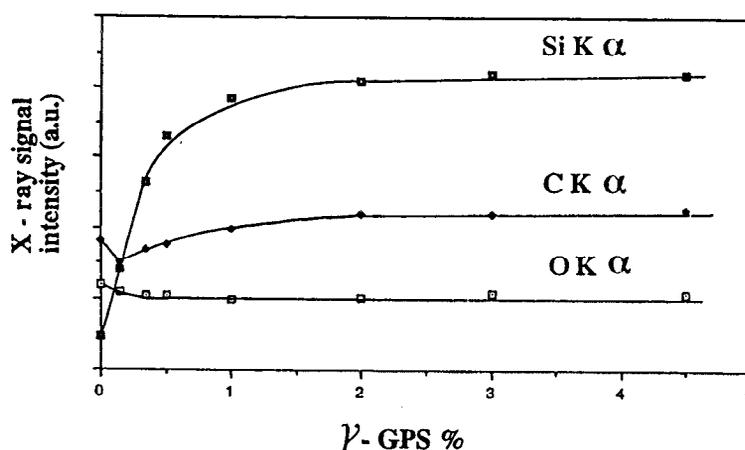


Fig. 8: Intensity variation of the Si K α , C K α and O K α emission line or bands of chemisorbed silane films on stainless steel substrates, as a function of the γ -GPS concentration in the solution.

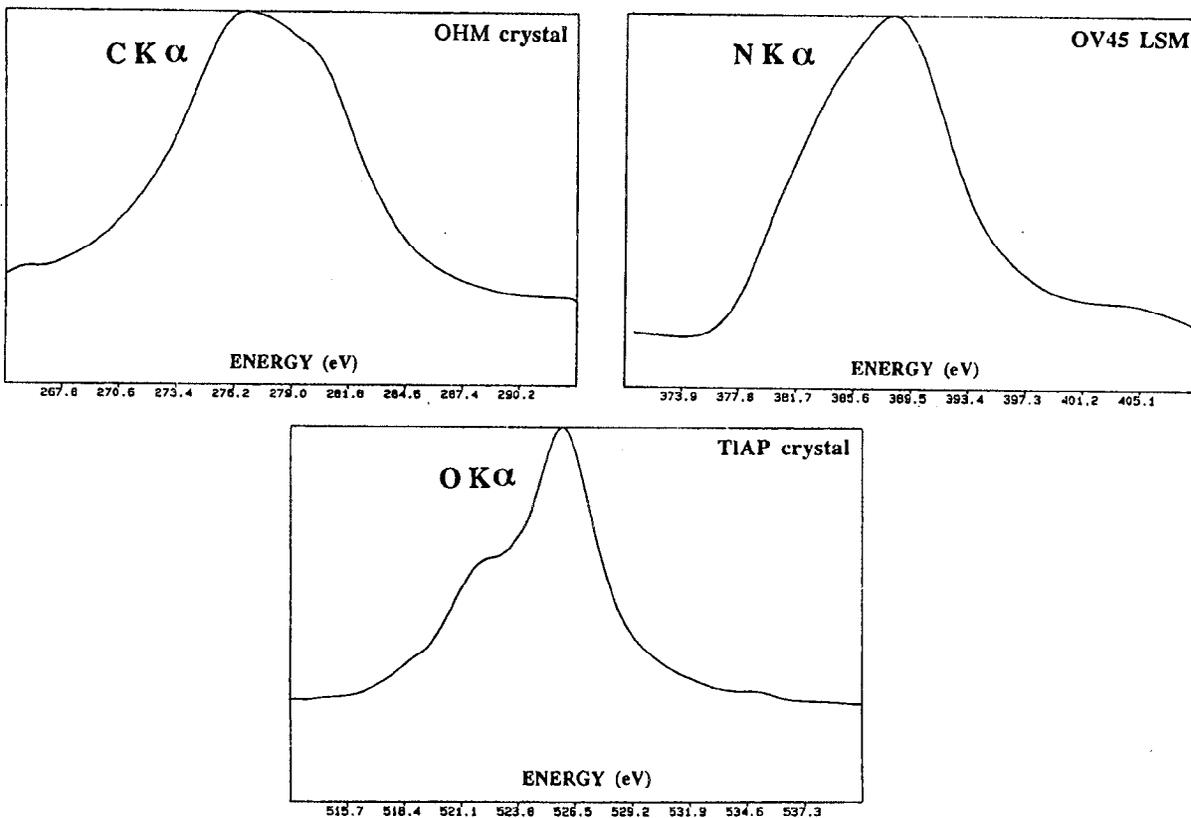


Fig. 9: C K α , O K α and N K α spectra of a polyimide sample (Kapton®).

of about 2 % and then remains fairly constant. For such experimental conditions, it is thought that the silane film deposited has grown in a rather well-ordered way onto the substrate surface, many hydroxyl groups originating from hydrolysis of methoxy groups having had the possibility in solution of reacting with the major part of chemical sites (OH functions) available at the material surface in order to form strong covalent metal-O-Si-bonds. It should be recalled here that such silanes are commonly used as coupling agents to enhance adhesion between polymeric and inorganic materials [8]. It should also be noted that LEEIXS data obtained in this work concerning the influence of the silane concentration are in quite agreement with the literature data [9] and that thicknesses of silane films which are chemisorbed on the metallic substrates under the experimental conditions used are in the range from 2 to 3 nm as that may be inferred from XPS measurements [10].

Lastly, it is interesting to show that LEEIXS analyses may be carried out in order to characterize polymer materials which possess a relatively high chemical and thermal stability. Obviously, it should be said, concerning such experiments, that the current density of the incident electron beam has to be chosen low enough ($\sim 0.1 \text{ mA.cm}^{-2}$) to avoid degradation of the organic materials under investigation. An example concerning polytetrafluorethylene (PTFE) samples has already been shown in a previous work [3]. In addition, figure 9 shows C K α , N K α and O K α spectra from a polyimide (Kapton®) sample. These experiments were performed with 3 keV electrons. N K α radiations were dispersed with a multilayer device (OV 45) while C K α and O K α did with OHM and TIAP crystals, respectively. Again these results confirm that LEEIXS is

capable of probing surface of some insulating and electron-sensitive samples without coating them with a conductive layer.

CONCLUSION

The above examples confirm that:

- (i) the potential of soft and ultra-soft x-ray spectrometry for characterizing surface and near-surface regions of solid materials, particularly via dispersion and detection of K_{α} radiations of light elements (B, C, N, O, F ... Si) has largely been under-estimated up to now,
- (ii) low-energy electron induced x-ray spectrometry (LEEXS), owing to its specific capabilities, is quite able to provide complementary information (particularly composition and thickness of very thin films) with respect to those supplied by more conventional methods (XPS, AES, ISS) currently used in the field. It should be noticed here that such performances may be attained even though LEEXS has an information depth (some tens of nanometers) greater than that of the other above-mentioned techniques.
- (iii) such a method of investigation can strongly help to choose the best processes and experimental conditions to be used in surface modification, and therefore to better understand how chemical, electrochemical or physical treatments affect the surface properties of various types of materials.

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