

Depth Profiles of Al/Mn/Si Multilayers

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Abstract. — An electron scattering model called IntriX associated to electron X-ray emission spectrometry (EXES) at high resolution is tested to characterize stratified samples. The ability of the model to simulate the X-ray intensity emitted by a surface layer and a buried layer in film/substrate systems is illustrated. The characterization of Al/Mn/Si multilayers by means of non destructive techniques (electron probe microanalysis (EPMA), Rutherford back scattering (RBS)) have been performed comparatively to the EXES measurements. The potentialities of the IntriX model combined to EXES to predict thicknesses is established by comparison with EPMA and RBS results.

1. Introduction

Characterization of thinner and thinner materials is of increasing interest. Analysis as a function of the sample thickness is possible by electron X-ray emission spectrometry (EXES) [1]. Indeed the analysed thickness depends on the incident electron energy E_0 and this parameter can be gradually increased from the energy threshold of the chosen emission, making a near surface region as well as the bulk to be analysed, in contrast with the electron probe microanalysis (EPMA). Moreover, due to the energy range of the incident electrons ($E_0 \leq 5$ keV) and of analysed soft X-rays, a strong peak to background ratio and weak self-absorption are present. All these factors make EXES to be an electron probe of high depth resolution.

Since Castaing's pioneering work, many models have been carried out in order to determine the intensity of the characteristic X-ray lines as a function of the sample and the incident electron energy. The aim of these models is to reproduce in an accurate way the distribution in depth of the X-ray intensity in a wide range of electron and X-ray energies. To achieve such interpretations the $\Phi(\rho z)$ function representing the distribution in depth of the primary ionizations generated per incident electron in the target must be described in an accurate way. These models are based on different mathematical descriptions of the function $\Phi(\rho z)$ [2–4].

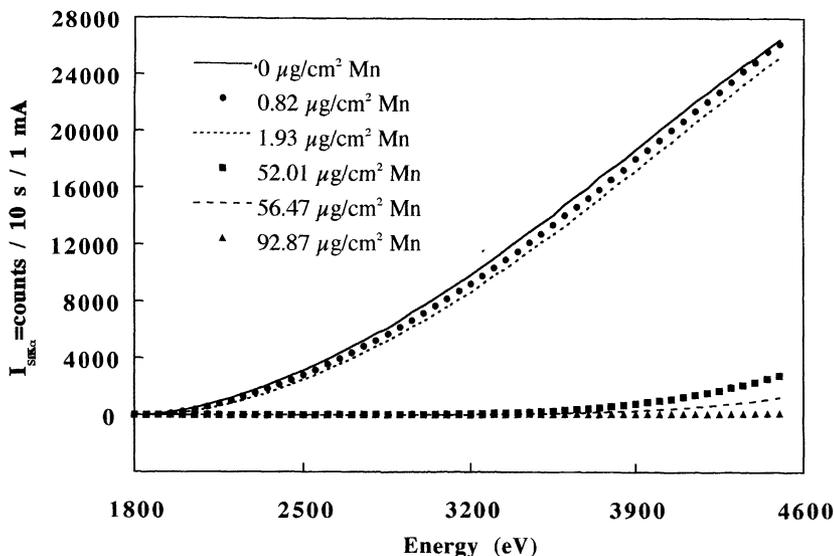


Fig. 1. — Experimental SiK α intensities emitted by the Si substrate covered by various manganese thicknesses.

A recent simulation model for electron probe analysis at high depth resolution was achieved. This model, called IntriX [5–7], takes into account physical parameters describing electron beam-matter interaction and consists in a numerical reconstruction of the depth ionization distribution. IntriX was used in order to carry out some quantitative analysis (composition, thickness) of homogeneous or layered samples, pure or complex, both in the thickness range of the EPMA and the nanometer range.

With the aim of studying the potentiality of the method, systematic measurements of the X-ray intensity emitted by a series of Al/Mn/Si samples of well defined composition and thicknesses are performed. From the X-ray measurements and the IntriX model, the thicknesses of layers are determined. We ensure that the samples are homogeneous by characterizing them by Scanning Electron Microscopy (SEM), EPMA and Rutherford back-scattering (RBS) techniques. Thicknesses measured from the EPMA by using the software Strata and RBS by using the RUMP and PYROLE softwares are compared to those obtained with IntriX.

2. Samples and Experimental

2.1. Samples

The silicon is chosen as substrate in order to achieve an optimal planarity of the deposits. A cleaning of the substrate surface is realized under ultra-sounds in alcohol bath. Then the silicon is introduced in the elaboration chamber of the instrument IRIS [8]. Multilayers are prepared *in situ* by thermal evaporation from molybdenum crucibles. The thicknesses of the deposited layers are controlled by a quartz micro-balance with an accuracy of $\pm 20\%$. After each deposit, the sample is transferred under ultrahigh vacuum from the preparation chamber to the analysis chamber.

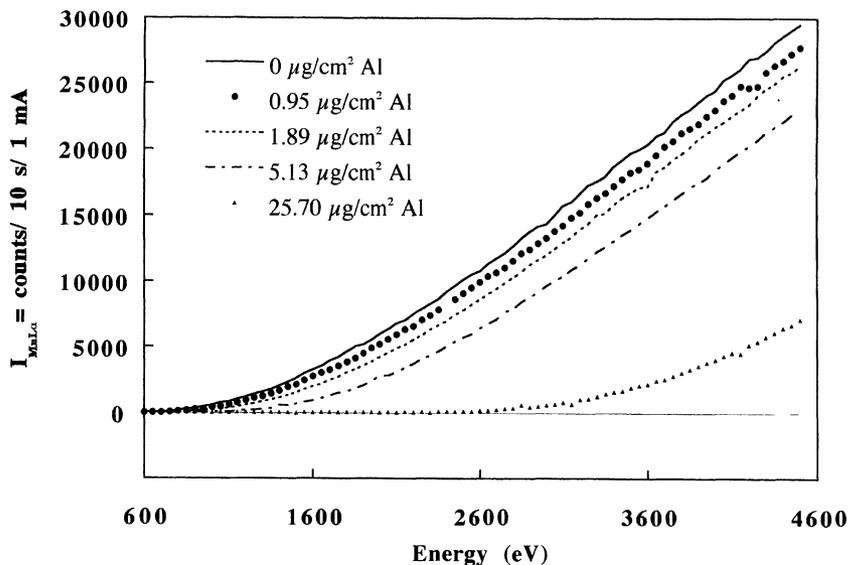


Fig. 2. — Experimental MnL α intensities emitted by a Mn substrate covered by various aluminium thicknesses.

2.2. Samples of Varying Thicknesses Studied by EXES

Excitation curves, *i.e.* intensity of a characteristic X-ray line as a function of incident electron energy, are measured for the sample and for a standard of known composition. In this case the standard is the pure element. Then the ratio of the intensity emitted by the sample and the standard, labelled k -ratio, is deduced for different accelerating voltages E_0 . The voltage E_0 varies from the emission threshold E_s up to 4.5 keV.

Si K α ($E_s = 1.84$ keV) intensity of the substrate is measured after successive manganese deposits whose thickness is varied from one nanometer to an hundred nanometers. We compared it to the intensity emitted by the bare silicon substrate. Then the intensity of the Mn L α emission ($E_s = 0.65$ keV) is measured after successive aluminium deposits varying of one nanometer to an hundred nanometers and compared it to the intensity of the thickest bare Mn layer. The thickness of Mn is sufficient for its properties to be those of the bulk in this energy range. Lastly the intensity of the Al K α emission ($E_s = 1.56$ keV) is determined for each aluminium deposit of one to a ten nanometers thick and compared to the intensity emitted by a bulk aluminium target. The sample involving all the layers is noted Al/Mn/Si.

The Figure 1 shows Si K α intensities measured from the substrate of silicon covered by manganese layers of increasing thicknesses and from the bare substrate. Due to the energy loss of the electrons in the covering material, the substrate intensity decreases with the increasing thickness of the superficial layer. On the other hand, the substrate intensity increases when the accelerating voltage increases. This behaviour can be interpreted in the following way. For small overvoltages ($U = E_0/E_s$), electrons have not sufficiently energy to ionize the material. When the energy of electrons after crossing the superficial film is greater than the emission threshold energy of the substrate, the ionization becomes possible and the intensity increases with the increasing voltage.

The Figure 2 shows the intensity of the Mn L α emission from the Mn(92.88 $\mu\text{g}/\text{cm}^2$)/Si sample covered by increasing aluminium thicknesses. It presents the same features than the

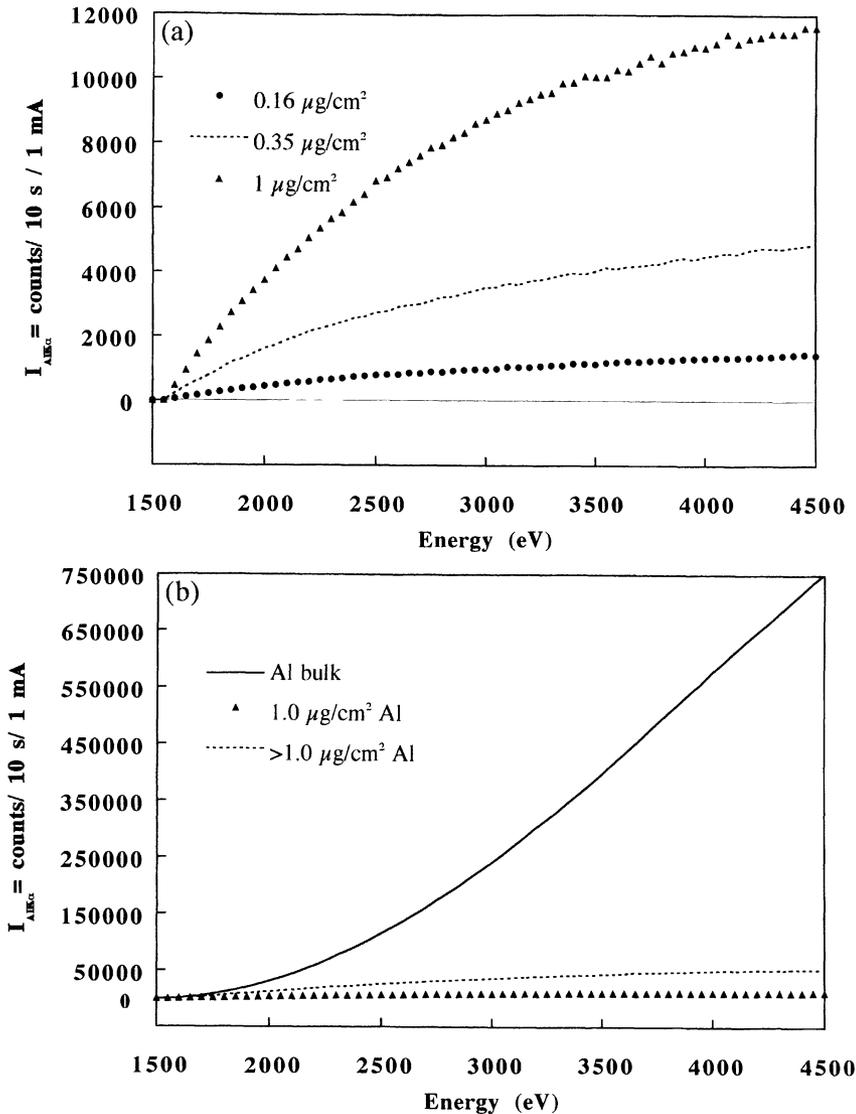


Fig. 3. — a) Experimental AlK α intensities emitted by aluminium films of various thicknesses deposited on the Mn(92.88 $\mu\text{g}/\text{cm}^2$)/Si sample. b) Comparison between AlK α intensities emitted by aluminium thin films and bulk deposited on the Mn(92.88 $\mu\text{g}/\text{cm}^2$)/Si sample.

SiK α emission. In the case of the Al K α emission (Fig. 3a), the intensity increases with the aluminium thickness. Nevertheless the shape of the Al K α excitation curve differs from previous ones and from that of the bulk material as shown in Figure 3b. For thin films, the intensity increases and saturates very rapidly. Indeed, when the incident energy is sufficiently high, the electrons excite the whole aluminium layer and reach the manganese substrate. This explains the intensity saturation.

The experimental k -ratios are presented in Figures 4 for the Si K α emission, in Figures 5 for the Mn L α emission and in Figures 6 for the Al K α emission. Energy and overvoltage scales

are indicated in figures. The experimental values are compared to k -ratios calculated by the IntriX model as discussed in Section 3.2. For small thicknesses of manganese (Figs. 4a, 4b), the Si $K\alpha$ k -ratio increases rapidly until it reaches a saturation value which is of the order of 0.9 for $0.82 \mu\text{g}/\text{cm}^2$ of deposited manganese. Discrepancies in the behaviour of the Si $K\alpha$ k -ratio appear for layers thicker than $7.43 \mu\text{g}/\text{cm}^2$. Until $U \leq 1.5$, this ratio is equal to zero because electrons, with near threshold energy, have lost all their energy before reaching the substrate. The same behaviour appears for the Mn $L\alpha$ emission. Discrepancies appear when the detected intensity is emitted by the superficial material. As we have accounted for it before, as soon as electrons reach the surface, the characteristic X-ray line is emitted and its intensity decreases because the film thickness is thinner than the analysed thickness (*i.e.* the thickness where primary electrons have energy greater than the emission threshold energy). The k -ratio never reaches zero as illustrated in Figures 6a, b, c. This is due to the influence of the backscattered electrons by the Mn substrate which induce extra ionizations and contribute to the Al $K\alpha$ emission.

2.3. Al/Mn/Si Sample Studied by Various Techniques

One of the multilayered samples has been characterized by three techniques. This multilayer is formed by more than $1 \mu\text{g}/\text{cm}^2$ of Al deposited on $92.88 \mu\text{g}/\text{cm}^2$ of Mn deposited on the silicon substrate. It is noted Al/Mn/Si.

2.3.1. EPMA

The Al/Mn/Si sample was analysed by EPMA. The Si $K\alpha$, Al $K\alpha$, Mn $K\alpha$ intensities have been measured. Indeed for medium atomic number and layer thickness of the order of 100 nm, the $K\alpha$ X-ray line is preferred to low energy lines. The incident electron energy is varied between 4 keV and 20 keV. The sample having been stored in air, a passivation layer of alumina is formed at the surface of the sample. The O $K\alpha$ intensity has been measured.

The k -ratios are reproduced Figure 7. Three voltages range are observed. Between 4 and 5 keV, only the Al $K\alpha$ emission is observed. Between 5 and 8 keV, the primary electrons excite the manganese layer and have sufficiently energy for exciting the Si substrate. Finally, between 8 and 20 keV, the electrons excite all the sample.

2.3.2. SEM

The homogeneity of deposits in surface and volume was checked by SEM for the Al/Mn/Si sample. This one is homogeneous as shown on the photograph (Fig. 8). During the SEM analysis, an EDS (energy dispersive spectrometry) X-rays analysis has been performed. It has revealed the presence of a small concentration of molybdenum. The molybdenum results from the crucible used to evaporate the multilayers.

2.3.3. RBS

The Al/Mn/Si multilayer was characterized using the RBS analysis with an $^4\text{He}^+$ beam of 2 MeV. The beam size was evaluated on an alumina to be $20 \times 20 \mu\text{m}^2$, with a beam intensity of 0.8 – 1.0 nA. The scattered ions were measured under a scattering angle θ of 175° with a solid angle of 15×10^{-3} sr. The geometry is given in the insert of Figure 9. The energy calibration is obtained by analysis of various known samples which give well defined energy levels: from Al_2O_3 and Si (low Z) to Mo and Ag (high Z).

Figure 9 presents the energy spectra of the scattered $^4\text{He}^+$ for three incident angles α of the beam in respect to the normal of the sample surface. For each spectrum the measurement doses is $1.5 \mu\text{Cb}$, *i.e.* 9×10^{12} ions. This is used to determine the actual position of the heavy

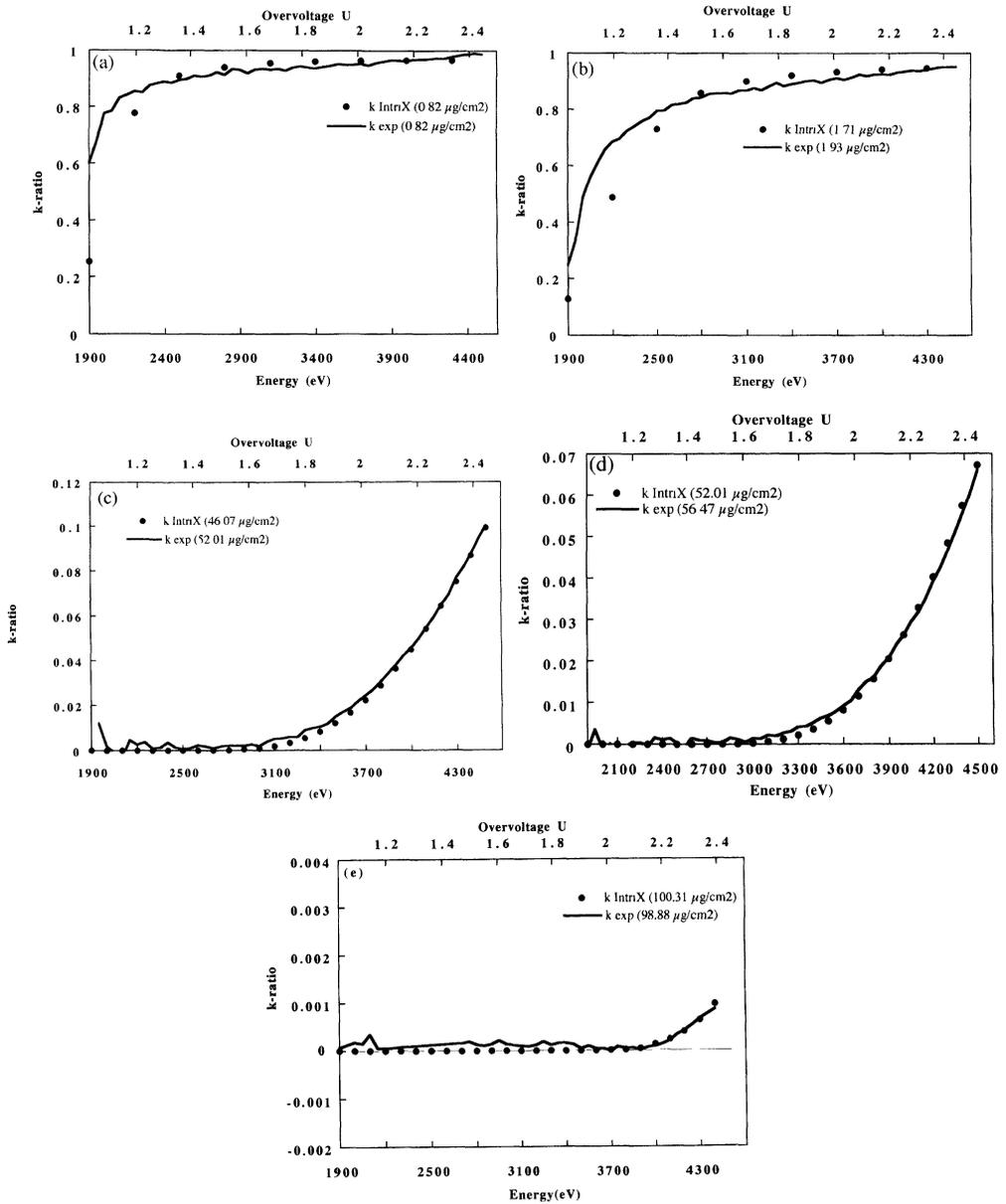


Fig. 4. — k -ratios of $\text{SiK}\alpha$ intensity emitted by a Si substrate covered by: a) $0.82 \mu\text{g}/\text{cm}^2$, b) $1.93 \mu\text{g}/\text{cm}^2$, c) $52.01 \mu\text{g}/\text{cm}^2$, d) $56.47 \mu\text{g}/\text{cm}^2$, e) $92.88 \mu\text{g}/\text{cm}^2$ of manganese. Line: experimental; dots: IntrIX values computed to match experimental.

impurity appearing at the high energy edge of the spectra. The spectra presented in Figure 9 display various features which may be described with increasing energy as follow:

- the silicon back-ground,
- a first small peak due to the aluminium top layer,

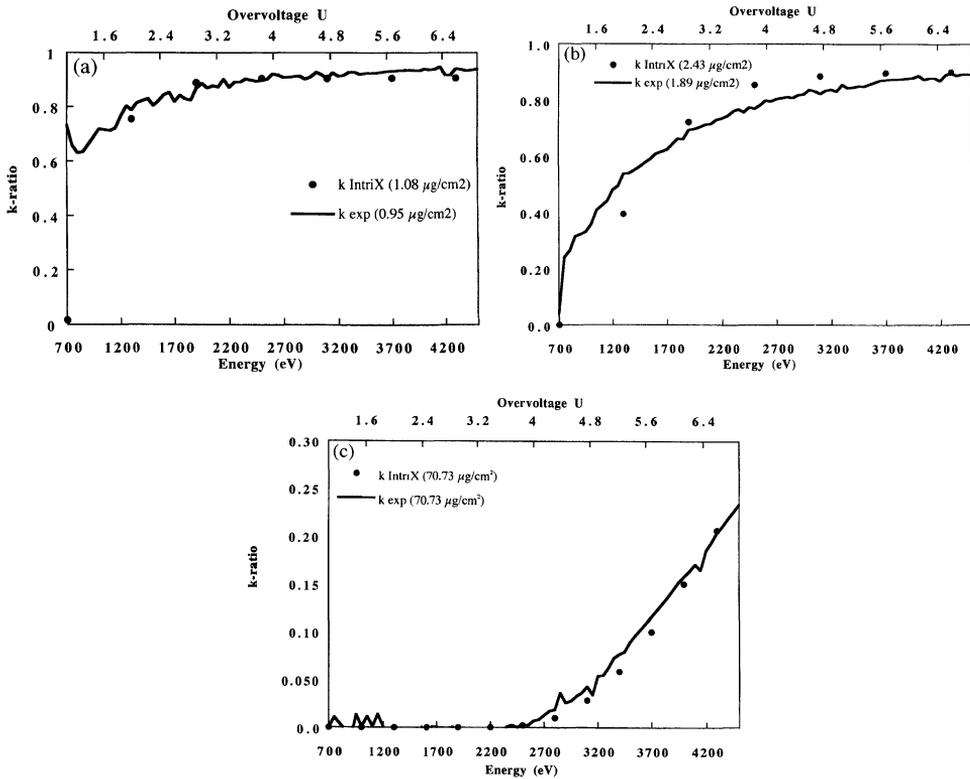


Fig. 5. — k -ratios of $MnL\alpha$ intensity emitted by a Mn substrate covered by: a) $0.95 \mu\text{g}/\text{cm}^2$, b) $1.89 \mu\text{g}/\text{cm}^2$, c) $25.70 \mu\text{g}/\text{cm}^2$ of aluminium. Line: experimental; dots: IntriX values computed to match experimental.

- a major one resulting from the intermediate layer of manganese,
- finally, a small contribution of some heavy impurity which can be identified as molybdenum from its position in the energy scale.

Apart from the aluminium peak the location of which is constant whatever the incident angle is, all others features are moving with the apparent thickness ($e/\cos \alpha$): the silicon edge and the manganese interface towards lower energies. For the molybdenum, the peak location is shifted to lower energies when the tilt angle increases from 0° to 50° : this means that the Mo is not at the surface.

When the ions are scattered in depth at an interface between two layers, they can scatter on the various species which are present. This results in many possible energies of the ions when they emerge from the sample:

for species i

$$k_i E_0 - E_{F,i} = [k_i S(E_0) + S(k_i E_0)] e_{\text{app}}$$

in which k_i is the kinematic factor, E_0 is the primary ion energy, $S(E)$ is the stopping power of ions with energy E and e_{app} is the apparent thickness $e/\cos \alpha$. The formula assumes that the interface is not too deep in the sample (the energy loss through the film must be small in

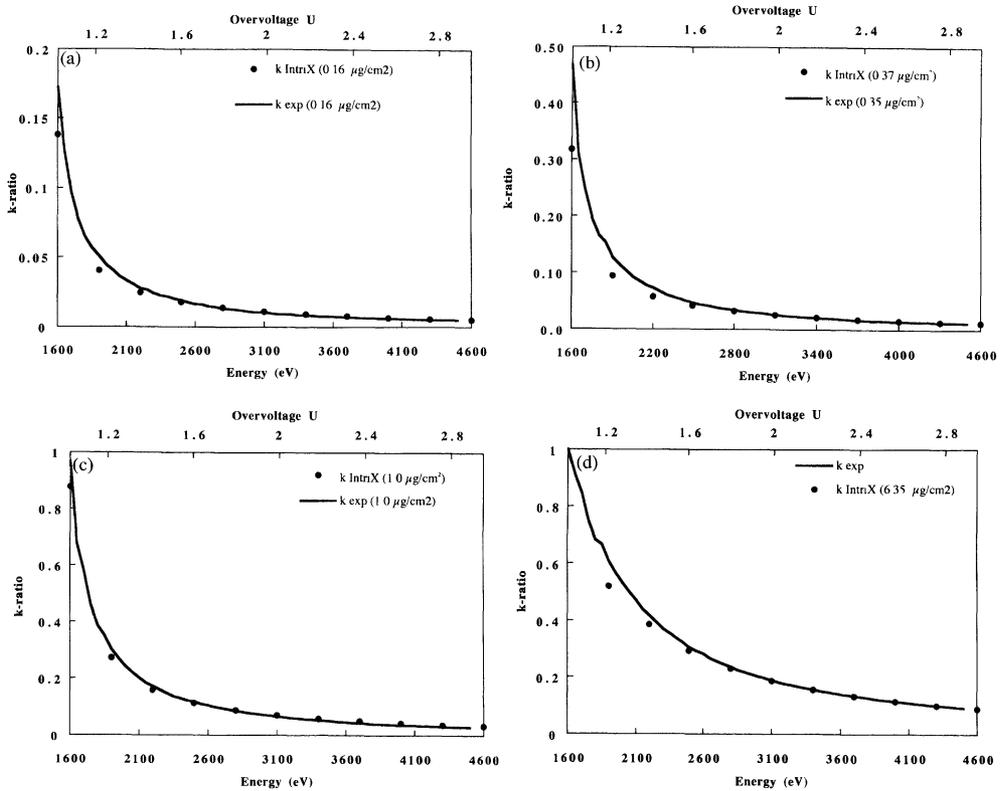


Fig. 6. — k -ratios of $AlK\alpha$ intensity emitted by an aluminium film deposited on Si substrate of: a) $0.16 \mu\text{g}/\text{cm}^2$, b) $0.35 \mu\text{g}/\text{cm}^2$, c) $1.00 \mu\text{g}/\text{cm}^2$, d) $> 1.00 \mu\text{g}/\text{cm}^2$ thickness. Line: experimental ; dots: IntrIX values computed to match experimental.

Table I. — Comparison of the calculated ($S(k_i E_0) + k_i S(E_0)$) and measured slopes of the energy variations obtained by RBS with the apparent thickness at the Mn/Si interface (* least square method in Fig. 10).

Element	$k_i S(E_0)$	$k_i E_0$	$S(k_i E_0)$	$S(k_i E_0) + k_i S(E_0)$	Slope*
Si	38.5	1128	822.9	121.4	150.0
Mn	51.1	1595	74.8	125.9	148.0
Mo	57.8	1693	73.1	130.9	62.6

comparison to the incoming energy of the ions, which is the case here: $\Delta E \approx 10 \text{ keV}$ versus $E \approx 2 \text{ MeV}$).

In order to determine the location of the molybdenum, the energy position of various features are shown in Figure 10 versus the apparent thickness. In every case the evolution of the energy is linear. Table I gives the values of the slopes in the case of the location of Mo at the interface Mn/Si. From these values there is a good agreement for Si and Mn but the Mo evolution is too small for the location of Mo at this interface. It is buried rather around the middle of the

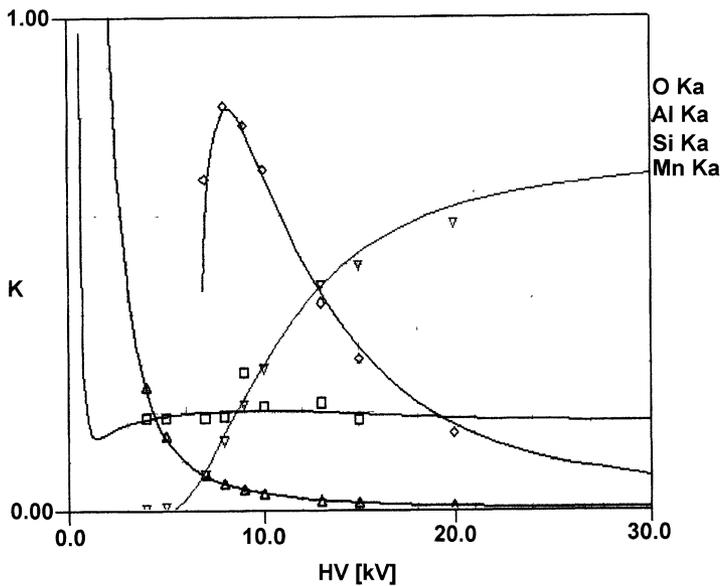


Fig. 7. — Variation of k -ratios of Si $K\alpha$ (Δ), Al $K\alpha$ (\triangle), O $K\alpha$ (\square) and Mn $K\alpha$ (\diamond) emerging from the sample Al/Mn/Si. Dots: experimental; lines: PAP model.



Fig. 8. — Surface morphology of the sample Al/Mn/Si; SEM photograph $E_0 = 12$ keV, magnitude = 10^5 .

Mn layer. Moreover this corresponds to the splitting in the Mn peak which is as well about half way of the layer.

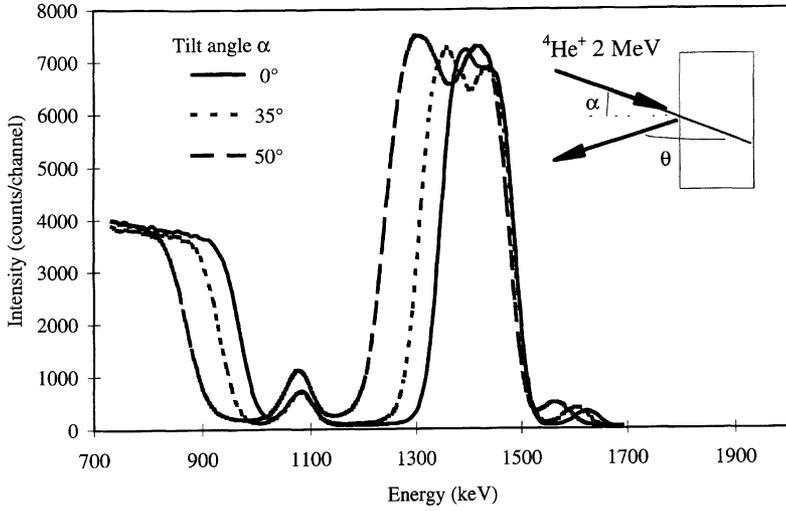


Fig. 9. — RBS spectra of the Al/Mn/Si multilayer.

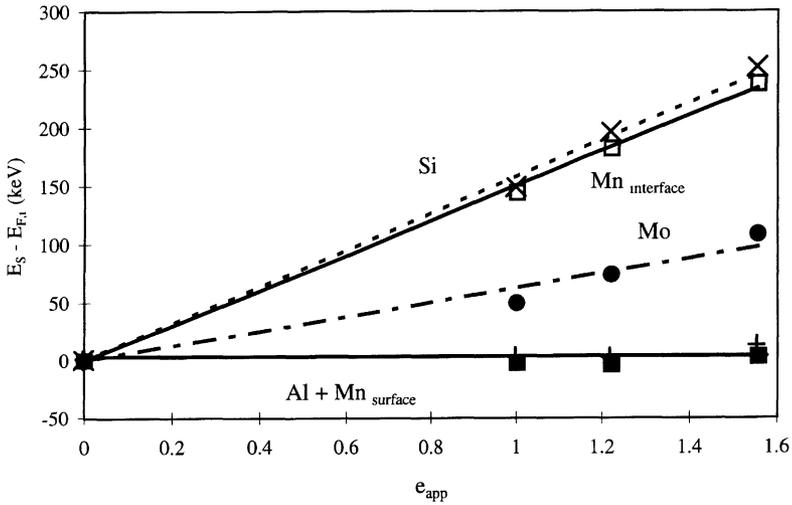


Fig. 10. — Energy shifts with the apparent thickness ($e_{app} = 0$ corresponds to the energy of the scattered ions on the surface of the different elements).

3. The Simulation Model IntriX and Comparisons with EXES Measurements

3.1. The IntriX Model

In this model, the target is imaginary sliced along planes parallel to the sample surface as shown in Figure 11. Electrons crossing an elementary layer of thickness dz , located at depth z , are back and forth scattered between two virtual planes. The depth distribution function $\Phi(\rho z)$ in this elementary layer results in the sum of the contribution of electrons which are

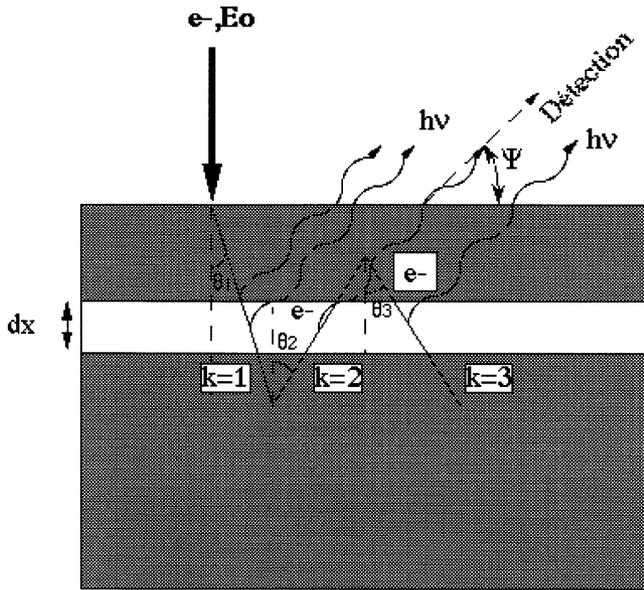


Fig. 11. — Representation of processes contributing to the X-ray emission used in IntriX. θ_i represents the deflection of i order electrons at depth z .

transmitted called first order electrons ($k = 1$), back-scattered called second order electrons ($k = 2$) and transmitted a second time called third order electrons ($k = 3$). The model takes into account the physical parameters which describe the electron beam-matter interaction such as electron transmission and backscattering coefficients, the corresponding energy and angular distributions and the ionization cross-section. The detailed description of the numerical reconstruction of the $\Phi(\rho z)$ is described elsewhere [5].

A basic parameter of the model IntriX is the electron projected range X_0 ; it corresponds to the sample thickness for which the number of transmitted electrons is attenuated by a factor $1/e$. The electron range is estimated within 20% error for any material ($Z \geq 4$) and a wide energy range ($0.5 \leq E_0 \leq 100$ keV) [9] due to the large dispersion of the experimental measurements.

3.2. Calculated and Measured Thicknesses

Incertitude on IntriX k -ratio due to 20% incertitude on the value of X_0 is about to 20%. In order to ameliorate the precision, the values of X_0 are adjusted in order to fit the IntriX k -ratios to the measurements. Increase of X_0 by 20% is used for Mn film and decrease by the same quantity for Al film.

The predicted k -ratios for different accelerating voltages are plotted comparatively to the experimental values in Figures 4 for the Si $K\alpha$ emission, in Figures 5 for the Mn $L\alpha$ emission and in Figures 6 for the Al $K\alpha$ emission.

The model reproduces in an accurate way the experimental data. Significant discrepancy between IntriX and experimental k -ratios only appears near threshold (*i.e.* very low overvoltage $1 < U \leq 1.08$) and for small mass thickness ($\leq 1 \mu\text{g}/\text{cm}^2$ for Al and $3 \mu\text{g}/\text{cm}^2$ for Mn). This

Table II. — Comparison between measured and computed thicknesses by *IntriX* from a) the *Si K α* emission in the case of manganese films of various thicknesses deposited on the *Si* substrate, b) *Al K α* and c) *Mn L α* emissions in the case of aluminium films of increasing thicknesses coating the *Mn* substrate.

a			b			c		
μ balance ($\mu\text{g}/\text{cm}^2$)	IntriX ($\mu\text{g}/\text{cm}^2$)	Δx (%)	μ balance ($\mu\text{g}/\text{cm}^2$)	IntriX ($\mu\text{g}/\text{cm}^2$)	Δx (%)	μ balance ($\mu\text{g}/\text{cm}^2$)	IntriX ($\mu\text{g}/\text{cm}^2$)	Δx (%)
0.82	0.82	0%	0.95	1.08	+14%	0.16	0.16	0%
1.93	1.71	-12%	1.89	2.43	+28%	0.35	0.37	5.7%
52.01	46.07	-11%	25.7	25.7	0%	1.00	1.00	0%
56.47	52.01	-8%					6.35	
92.87	100.31	+8%						

is explained by the strong variation of the ionization cross-section near threshold. Moreover, the energy dependence of the angular deflection of the first order electrons is not taken into account in the model. This leads to an under-estimation of the intensity produced near the surface to which one adds the experimental uncertainty. For overvoltage greater than 1.08, the accordance is good. Then it is possible from experimental *k*-ratios to obtain in a reliable way the deposited thicknesses if the density is known. The densities of manganese and aluminium are set equal to the value of the bulk pure element.

The thicknesses obtained with *IntriX* are reported in Table II and compared to those measured by the micro-balance. The thicknesses of manganese calculated from the *Si K α* emission are reported in Table IIa and those of aluminium calculated from the *Mn L α* and *Al K α* emissions respectively in Tables IIb and IIc. The values obtained with *IntriX* are in good agreement with those measured by means of the quartz micro-balance even for the smallest deposits. The difference is of the order of 10% for thicknesses between one and hundred nanometers. The discrepancy is the greatest for the aluminium thickness obtained from the *MnL α* emission. In this energy range and for L lines of transition elements of the first series, the mass absorption coefficients (MAC) are known with a bad accuracy when approaching an absorption discontinuity and the *L α* X-ray lines are strongly self-absorbed. This can explain that deviation between *IntriX* and the micro-balance increases (it reaches 28% in this case).

IntriX is well suited to treat film/substrate systems for $E_0 \leq 5$ keV and for overvoltages as low as 2. Film thicknesses are generally determined with an error lesser than 10% even in the case of nanometric deposits.

4. Discussion of Results Obtained by the Different Methods for the Al/Mn/Si Sample

Comparison between *IntriX* and *Strata* The thicknesses of layers are obtained from EPMA *k*-ratios by using the program *Strata* [10] resulting in the cooperation between J.-L. Pouchou (ONERA) and the SAMx company. It is based on the PAP model [2]. As illustrated in Figure 7, the PAP model restores well the experimental results for the layers and for the substrate. The determination of the layer thicknesses is in good agreement with this obtained with *IntriX* (Tab. III). The deviation is of 4% for Mn and 2% for Al. From *Strata* the thickness of superficial alumina is of one nanometer.

Table III. — Comparison between measured by the quartz micro-balance and computed mass thicknesses obtained with *IntriX*, *Strata* (EPMA), *RUMP*, *PYROLE* (RBS).

	Microbalance	IntriX	Strata	RUMP PYROLE
Thickness of Mn ($\mu\text{g}/\text{cm}^2$)	92.88	100.31	96.59	109.97
Thickness of Al ($\mu\text{g}/\text{cm}^2$)		6.35	6.48	6.48
Thickness of Al ₂ O ₃ ($\mu\text{g}/\text{cm}^2$)	-	-	0.39	-

Comparison between IntriX and RBS For RBS, the thicknesses are determined by using the RUMP and PYROLE softwares. A greater dispersion is obtained for the buried layer than for the superficial layer (Tab. III). Thus, for the manganese the value exceeds of 16% the microbalance value, of 12% that obtained with Strata and 9% that obtained with IntriX. The thickness of the aluminium layer is identical to that obtained with Strata and IntriX. The molybdenum buried at about $52 \mu\text{g}/\text{cm}^2$ under the manganese surface is $1.3 \mu\text{g}/\text{cm}^2$ thick.

The discrepancy between RBS and EXES can be explained as the following way. The geometrical conditions are chosen so that the incidence angle of the electron beam with respect to the surface is 30° . Due to the electric field, electrons go the shorter path so that the average incidence angle is lower than the geometric angle. A 10° decrease of the electron incidence angle leads to a 4% increase of the thickness. Thus a systematic error must be taken into account on the determination of the thickness. By taking into account experimental and systematic errors deviations between IntriX and RBS are within the experimental precision.

The molybdenum has not been taken into account in IntriX and Strata calculations. Indeed the Mo thickness is small ($\approx 2\%$ in mass thickness) in comparison to that of Mn and its contribution in the determination of the Mn thickness is slight. Moreover, the electrons are more back-scattered in Mo than in Mn (back scattering coefficient 0.304 for Mn and 0.395 for Mo [11]). When Mo is taken into account, a slight lost in electron number occurs and the number of ionizations created in the Si substrate is slightly decreased. On the other hand, the Si $K\alpha$ emission generated into the sample is more absorbed by the Mn ($\mu/\rho = 2225 \text{ cm}^2/\text{g}$ [12]) than by Mo ($\mu/\rho = 1493 \text{ cm}^2/\text{g}$ [12]) and this contributes to a slight increasing of the intensity of the Si $K\alpha$ emission emerging from the sample. Consequently, the two last effects vary in opposite way and balance partially. This again justifies that the Mo contribution can be neglected.

5. Conclusion

The high depth resolution of EXES with respect to EPMA enables to achieve quantitative analysis of thin superficial or buried layers between one and an hundred nanometers thick. This necessitates that experimentation is performed with low electron energy and overvoltages as low as 2. As illustrated by the presented examples, IntriX is able to predict with accuracy the k -ratios from various samples and film thickness is determined with a typical 10% error (30% error at worst when $L\alpha$ X-ray lines of the first series transition elements are used).

For the Al/Mn/Si sample, EXES gives results in agreement with the other techniques of analysis in particular with RBS determination whose the absolute error is known to be lower than 5%. This proves the capability of EXES to characterize complex materials. Two improvements are in project. The use of a Pierce gun will eliminate the systematic error due to the

perturbation of the incident electron beam by the electric field. Lastly, an accurate knowledge of the electron range X_0 will lead to an improvement of the IntriX model and will contribute to increase the accuracy of the method.

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