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On the Improvement of SIMS Technique by the Use of MCs^+ Molecular Ions

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Abstract. — The SIMS MCs^+ method, consisting of detecting the molecular ions formed by the element of interest M and Cs^+ ion, emitted under Cs^+ bombardment is discussed in this work. A strong reduction of matrix effects has been observed in all the investigated samples. Moreover linear calibration curves can been obtained with good accuracies by plotting the relative matrix concentrations against the corresponding signal intensity ratios. A comparison with XPS results obtained from the analysis of a Fe on Zr on SiO_2 structure has been also reported. In addition good depth resolution and near surface pre-equilibrium region reduction have been observed on MCs^+ profiles.

1. Introduction

Secondary Ion Mass Spectrometry (SIMS) is a powerful technique for element profiling because of important attributes as: capability of detecting all the elements, high dynamic range, low detection limits and a depth resolution which approaches to 1 nm. Nevertheless the non-linear compositional dependence of the ionization probability, phenomenon known as "matrix effect", often inhibits the possibility of obtaining reliable quantitative results [1]. Moreover, the secondary ion yields are heavily affected by the presence of reactive species (oxygen and halogens for positive ions, alkali metals for negative ions). For elements with dilute concentration in a uniform matrix, quantitative results within accuracies of 10% can be easily obtained by using ion implanted reference standards. On the other hand, the quantitative evaluation of matrix composition is not straightforward [2] and a comparison with other, more quantitative, techniques and simulation programs are necessary [3].

An analytical method, based on molecular ions detection, has shown to be useful for compositional analysis [4].

Molecular ions monitoring is often employed in SIMS to improve the detection of ion species which show poor dynamic ranges or are affected by mass interference. For example AsC^- [5] is usually detected instead of C^- in GaAs because the latter has a high background arising from residual gas species in the analysis chamber.

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In the approach discussed in this work, the diatomic molecular ions MCs^+, obtained from the emitted target element, M, and the primary Cs^+ ion, are monitored. This mode has been firstly and successfully employed for detecting species as zinc and inert gases which usually show very poor atomic ion yields [6, 7]. The advantage of this mode, however, lies in the finding that MCs^+ ion signals show a little matrix dependence, i.e. a linear dependence of molecular ion yields on concentration.

The molecular ions are probably formed *via* a recombination mechanism of the neutral M atom coming out at the surface and the implanted Cs^+ [4, 8]. The mechanism has not been yet completely understood due to the lacking of useful experimental parameters as the cross sections values for reactions in solid matrices and the binding energies of free diatomic MCs molecules. Up to now a more detailed study trying to correlate the surface cesium concentration, the surface work function changes and the MCs^+ yields, has not been faced [9].

Moreover, the reduced matrix influence on MCs^+ yield is not observed for all matrices, indeed, it depends on material as well as primary beam conditions [8]. The matrix dependence of the signal is mainly due to changes in the stationary cesium surface concentration (depending on the specimen sputtering yield) which reaches a maximum value at near normal incidence (0° with respect to the normal to sample surface) and becomes negligible above 60°. When the stationary concentration of cesium is high enough, it causes a decrease in the surface work function increasing the probability of efficient neutralization by electron tunneling, causing a depression of the MCs^+ signal. This is strongly evident in silicon and aluminum matrices where the cesium retention is greater. For other materials such as germanium and gallium arsenide [8], the molecular ion yields are weakly affected by incident angle changes even under 60°, suggesting that at each angle the stationary Cs concentration at the surface is always small leaving the work function a constant.

In the present work a collection of examples of measurements performed in our laboratory are reported. They show the analytical applicability of this non-conventional SIMS technique.

Beside the advantages for compositional analysis the aim of this work is also to show the excellent capability of profiling very thin layer, attaining a good depth resolution and a reduction of near surface pre-equilibrium region. A comparison with X-ray Photoelectron Spectroscopy (XPS) results from a Fe/Zr bilayer is also reported.

2. Experimental

All SIMS measurements have been performed by means of a CAMECA ims4f magnetic sector instrument.

Standard SIMS measurements have been performed by using O_2^+ and Cs^+ primary ions and detecting $M^\pm$ secondary ions. MCs^+ detection has been obtained under Cs^+ ions bombardment.

During positive secondary detection (both M^+ and MCs^+) the beam impinged on the surface with an energy of 5.5 keV and an angle of incidence of 42° with respect to the sample surface normal.

In the negative detection scheme a Cs^+ beam impacted the surface at 14.5 keV and an angle of 25°.

We have monitored also M^+ secondary ions under Cs^+ bombardment in order to compare monoatomic and molecular ion signal shapes under identical experimental conditions.

A well shape focused beam has been rastered across a square area ensuring a flat erosion. The scanned area sizes ranged from 150 μm to 250 μm according to the different erosion rate conditions.

In order to avoid crater edge effects the secondary ions have been collected from the center of the eroded area by means of an optical aperture with diameters ranging from 8 to 30 μm.

XPS analyses have been performed by means of a VG Scientific Escalab 210 D spectrometer operating with a non-monochromated Al K_α radiation with a 90° take-off angle.

The depth profile has been obtained sputtering the surface sample by a 3 keV argon beam. A survey scan spectrum (0 – 1100 eV) and narrow scans in the C1s, O1s, Zr3d, Fe2p regions have been recorded for all the sputtering levels.

Pass energies of 50 eV and 20 eV in the fixed analyzer mode have been employed for the survey and the narrow scans respectively. All the spectra have been corrected for sample charging. The integrated peak areas and the Wagner atomic sensitivities, corrected by the spectrometer response function, have been used for quantitative analysis.

3. Results and Discussion

If a linear dependence on matrix composition is observed, a linear calibration curve can be obtained. An example of this is given by the analysis of five $In_xGa_{1-x}As$ layers grown by Molecular Beam Epitaxy (MBE) on GaAs substrates with thickness of about 1 μm. Figures 1a and 1b show the plots of the relative indium concentrations against the $InCs^+/AsCs^+$ and In^+/As^+ ratios, respectively. The concentration values were known from Rutherford Backscattering Spectrometry (RBS) and X-Ray Diffraction (XRD) measurements. SIMS analyses have been performed by using the same Cs^+ beam at 5.5 keV for all the samples but they have not been made in the same run. To account for the different experimental conditions (differences in the energy bandpasses, erosion rates etc.) the yields ratios have been normalized to the $GaCs^+/AsCs^+$ ratios in the GaAs substrates. The MCs^+ results show a clearly linear dependence and an accuracy of $\pm 3\%$ has been estimated from the plot. On the contrary, the x *vs.* In^+/As^+ plot deviates from linearity. Similar results have been observed for $Al_xGa_{1-x}As$ samples [4] and for $Al_xIn_{1-x}As$ samples. These results suggest the possibility of drawing linear calibration curves for III-V semiconductors and their related (ternary or quaternary) compounds from which accurate calibration factors can be extracted.

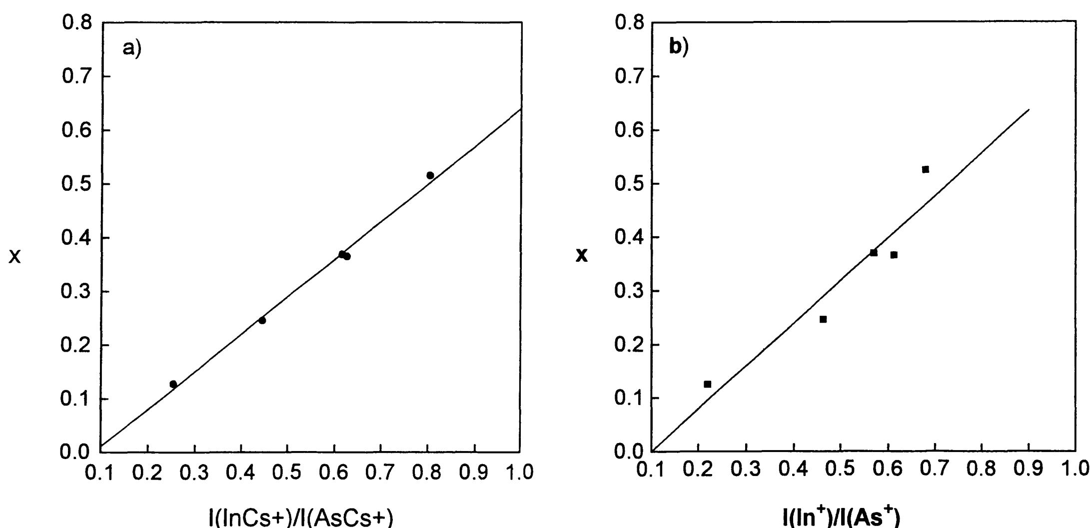

Fig. 1. — a) Plot of the relative In concentration (x) against the $InCs^+/AsCs^+$ ratio for five $In_xGa_{1-x}As$ MBE layers. b) Plot of the relative In concentration (x) against In^+/As^+ for the same samples.

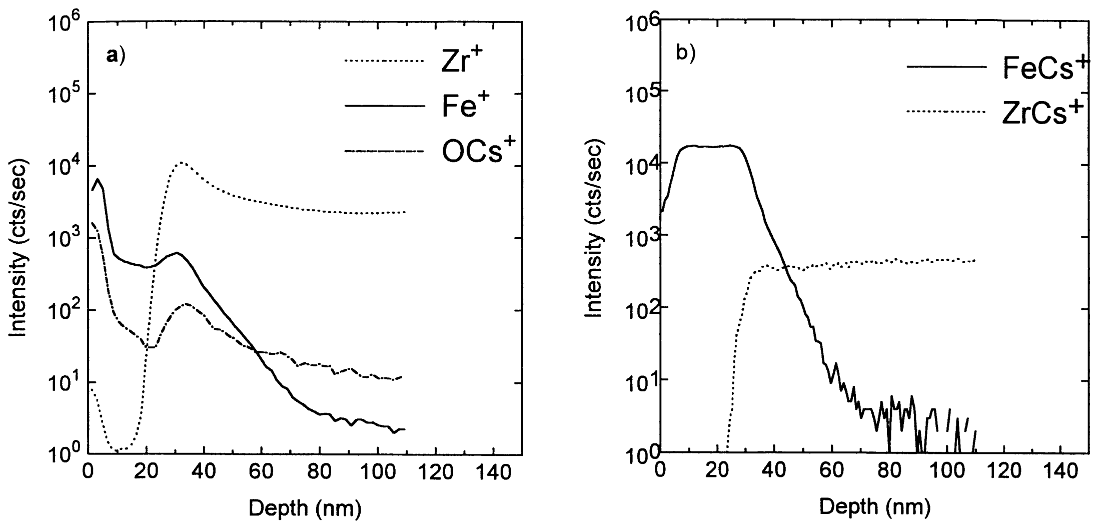

Fig. 2. — a) Fe^+ and Zr^+ signals plotted *vs.* depth, obtained from a 30 nm Fe on 500 nm Zr on SiO_2 substrate using the standard SIMS mode, the oxygen distribution (recorded as OCs^+) is also reported. b) Fe and Zr depth profiled performed by using the MCs^+ mode.

As mentioned in the first section it has been suggested [8] that, in order to reduce matrix effects, angles below 60° (with respect to the surface normal) are mandatory, this is mainly due to the sputtering yield dependence of the MCs^+ signals.

In the spectrometer used in our experiments the choice of angle is not arbitrary, indeed sample can not be tilted with respect to the incident beam. The angle of incidence is strictly related to the primary energy and to the ±4.5 kV secondary ion extraction potential [10].

The minimum achievable potential when a Cs^+ beam is used is of 10 kV, so that during M^- detection, the primary energy is of 14.5 keV with an impact angle of 25°. In MCs^+ mode the secondary extraction voltage is reversed resulting in an impact energy of 5.5 keV and an angle of 42°. Under O_2^+ bombardment lower energies (down to 1 keV) and more grazing incidence can be reached.

Hence in the present work the MCs^+ detection scheme is obtained at an angle (42°) which lies below the indicated limit (60°).

Nevertheless matrix reduction is still observed for all the samples investigated in this work, implying that the surface cesium concentration is not high, enough to induce a work function decrease.

Moreover the MCs^+ signal are poorly influenced by the presence of high concentrations of reactive species such as oxygen which usually leads to distorted signals.

This is clearly shown in what follows, representing a clear example of the great advantages of the MCs^+ technique.

We have analyzed a sample consisting of a 30 nm Fe layer on 500 nm Zr layer on a SiO_2 substrated, grown by ion beam sputtering technique.

Figure 2a displays the Fe^+ and Zr^+ signals recorded as function of depth. In the same plot we report the oxygen behavior (recorded as OCs^+), signals from the substrate are not reported.

It can be observed that Fe^+ and Zr^+ signals show a strong dependence on oxygen distribution, yielding spurious peaks located at the surface and the interface, corresponding to regions with a higher oxygen content.

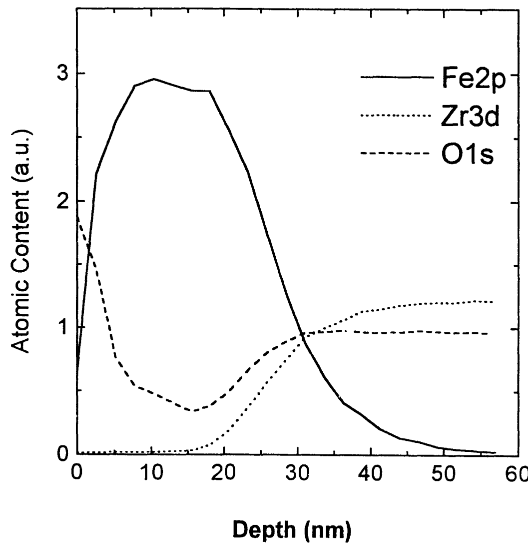

Fig. 3. — Fe, Zr and O depth profiles obtained by XPS measurements.

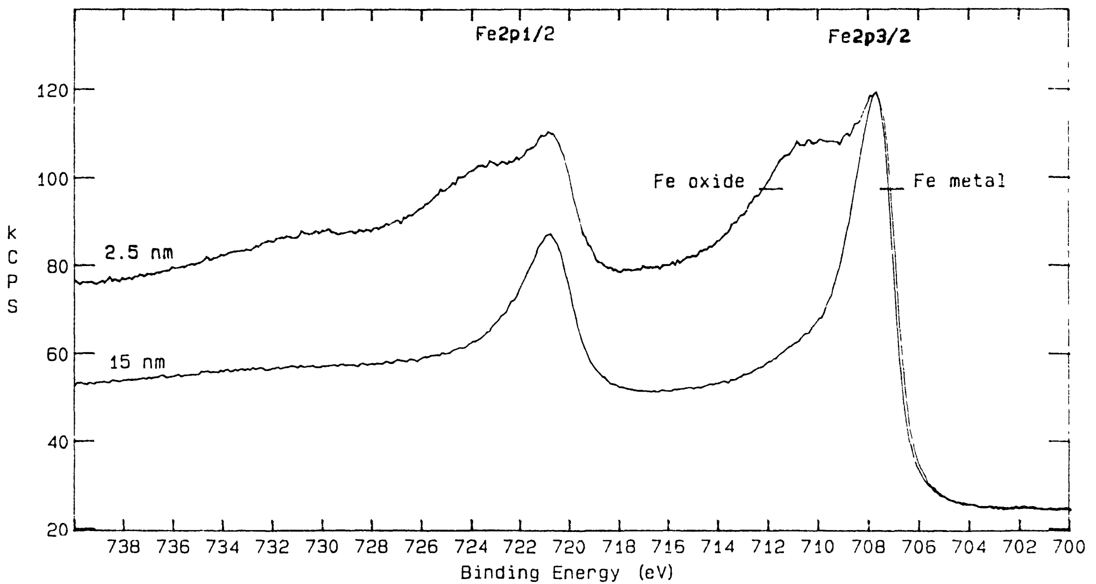

Fig. 4. — Comparison between the XPS spectra of Fe2p 1/2,3/2 recorded on the surface (2.5 nm) and in the Fe layer (15 nm).

Conversely the $FeCs^+$ and $ZrCs^+$ signals are flat and independent of oxygen as can be noted in Figure 2b. The electron affinity of zirconium (0.43 eV) is greater than that of iron (0.16 eV) so that it has an higher negative elementary ion yield, which explains the lower corresponding $ZrCs^+$ intensity.

MCs^+ results are confirmed by XPS analysis. Figure 3 displays the Fe, Zr and O relative atomic contents as recorded by XPS and plotted against the depth. The profiles resemble to those

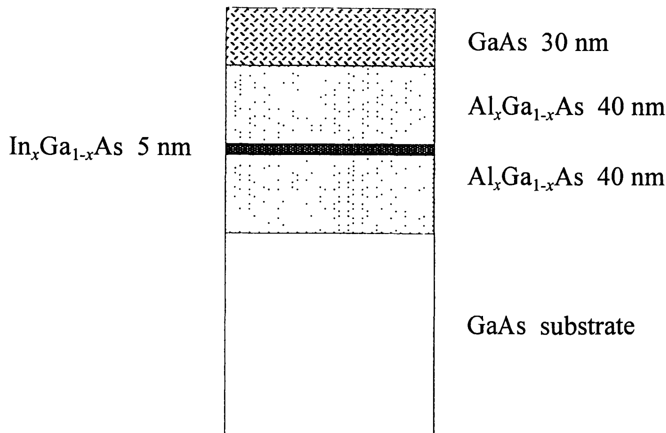

Fig. 5. — Layer sequence of the MOCVD structure in which the investigated 5 nm $In_xGa_{1-x}As$ quantum well was embedded.

obtained by MCs^+ technique, also, the oxygen distribution at surface and interface is confirmed. In addition Figure 4 reports the Fe2p(1/2,3/2) peaks recorded at 2.5 nm (near the surface) and at 15 nm (in the Fe layer). It can be noted that Fe has a metallic and an oxide component at the surface, proving that iron oxide is formed in this region, in the layer the Fe peak has only a metallic component.

Also the Zr3d (not reported here) peaks show an oxide component at the interface meaning that an oxide is present in this region.

As shown in Figure 2b a good depth resolution is achieved since a low energetic beam (5.5 keV, 42°) has been used. We have estimated an interface transition width on Fe signal (considered as the width where the signal drops from 90% to 10%) of 8 nm.

Use of Cs^+ rather than O_2^+ with the same primary energy, leads to reduced collisional distortions due to the higher mass of the former which consequently has a smaller projected range. This has some advantages when sharp features must be profiled especially when they are located near the surface. The lower Cs^+ penetration depth causes a less extended pre-equilibrium variation which usually causes distortion of the elemental distribution near the surface.

An example of sharp structure profiling is given by an $In_xGa_{1-x}As$ "quantum well" of nominally 5 nm grown by Metal-Organic Chemical Vapour Deposition (MOCVD). The thin layer is embedded in a more complex structure consisting of several layers disposed in the sequence shown in Figure 5.

Figure 6a displays the Al, Ga, As and In depth profiles obtained by using a 5.5 keV O_2^+ beam, the shift between the maximum of In signal and the minimum of Al is due to the different ranges of the primary beam in the different materials. Figure 6b reports the comparison with the $InCs^+$ signal yielded by the same structure, the signals have been normalized at the same value and the differential shift has been taken into account. Although profiles show a nearly similar broadening of the decay edges, the $InCs^+$ rising edge is better resolved.

The $In_xGa_{1-x}As$ layer can be considered a thin δ layer [11], i.e. it is an instrumental response function whose shape is mainly determined by mass transport effects induced by the incident ion beam. In this case the use of a conventional procedure consisting of multiplying the emitted ion intensity by an independent sensitive factor leads to an apparent concentration quantification which does not corresponds to the reality. Indeed only a sheet concentration can be deduced.

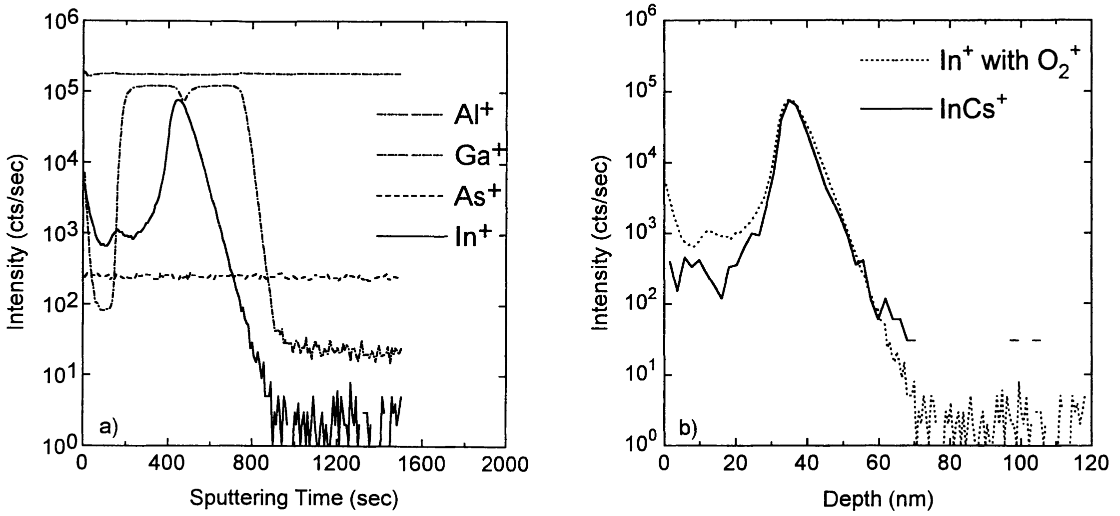

Fig. 6. — a) Al, Ga, As and In depth profiles of the MOCVD structure, obtained by using a 5.5 keV O_2^+ primary ion beam (standard mode). b) Comparison between the In depth profiles of the quantum well as obtained by the standard mode and the MCs^+ mode with the same energy and angle of incidence.

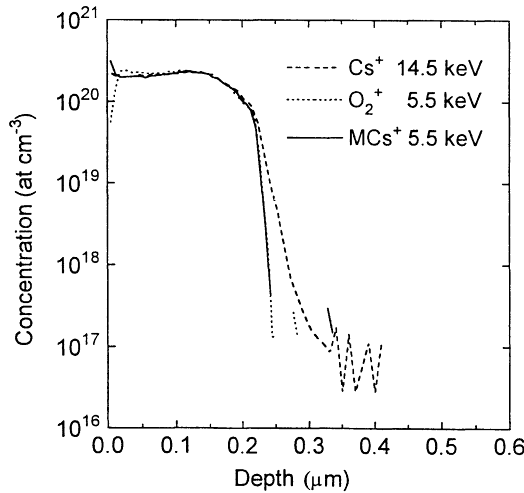

Fig. 7. — Comparison of depth profiles obtained from the same arsenic distribution in silicon by using a 14.5 keV Cs^+ ion beam, a 5.5 keV O_2^+ beam under high mass resolution condition and a 5.5 keV Cs^+ beam in the MCs^+ mode.

Nevertheless certain features (excluding problems arising from sample topography) in the profile can be related to the growth process.

A segregation phenomenon can be identified by the heel observed at the rising edge of the $InCs^+$ profile, and the In accumulation at the first $GaAs/Al_xGa_{1-x}As$ interface.

The last example is a typical ask of semiconductor industry regarding dopant profiling of As in Si used for shallow n-p junction.

Usually good detection limits of As in silicon are obtained by monitoring As^- ions using a Cs^+ beam; better results can be achieved from the $SiAs^-$ detection. The 14.5 keV primary beam energy — mandatory in a CAMECA ims4f when using Cs^+ —, however, causes a pronounced signal broadening which is very detrimental for the depth resolution.

To have a better depth resolution an O_2^+ beam with low energy must be used, mass interference of As^+ with $(^{30}Si^{29}Si^{16}O)^+$ molecular ion makes the analysis more complex, reducing the detection limits. Moreover, under oxygen bombardment, a transient region due to formation of an oxide layer at the surface is observed. It can be reduced by further lowering the energy but loosing in sensitivity.

Conversely the $AsCs^+$ signal is not affected by mass interference and transient region is reduced with respect to the oxygen analysis under same energy conditions. Figure 7 shows the results attained by the three different modes. As-mode shows better detection limits but is affected by signal collisional broadening. On the contrary the $AsCs^+$ signal and that obtained by using the oxygen beam at the same energy (5.5 keV) have a better depth resolution at the decay edge and comparable detection limits (about 2×10^{17} at cm^{-3}). The surface transient region of the As^+ signal is not observed on the $AsCs^+$ yield.

4. Conclusions

The MCs^+ method of SIMS analysis has been applied by using a magnetic sector spectrometer. In such an instrument, when using a Cs^+ beam, the more achievable grazing angle of incidence with respect to the surface normal (42°) lies below the indicated limit condition (60°) for matrix effect reduction.

Nevertheless for all the analyzed samples strong reduction of matrix effect has been observed, even in presence of high reactive elements concentrations. These results suggest that for the investigated samples the sputtering yield dependent cesium concentration remains small and does not affect the surface work function.

Under these condition linear calibration curves for an accurate quantification can be attained. An example of this has been given for $In_xGa_{1-x}As$ layers.

Good depth resolution and reduction of transient near the surface region has been also observed.

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