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#### LIMITATIONS ON AES QUANTITATIVE ANALYSES OF PLASMA DEPOSITED CERAMICS

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**Abstract** - Difficulties encountered in using AES for quantitative measurements have been evaluated with three plasma deposited materials : amorphous hydrogenated silicon carbide  $a\text{-Si}_x\text{C}_{1-x}\text{H}$ ; amorphous hydrogenated silicon nitride  $a\text{-SiN}_x\text{H}$ ; crystallized hydrogenated aluminium nitride  $\text{Al}_x\text{N}_y\text{H}$ . For  $a\text{-Si}_x\text{C}_{1-x}\text{H}$ , the values of composition  $x$  calculated from Peak/Background and Area/Background ratios are not very different for materials near to stoichiometry or rich in silicon. A divergence on results is noticed for  $a\text{-Si}_x\text{C}_{1-x}\text{H}$  films with carbon-rich contents and for  $a\text{-SiN}_x\text{H}$  films. This is attributed to broadening effects seen on the KVV peak of carbon and on both LVV and KLL peaks of silicon. The most important problem in  $\text{Al}_x\text{N}_y$  thin films quantitative Auger analysis is to find suitable reference samples. Available ones are silicon nitride and pure aluminium. The aluminium KLL Auger spectrum is characterized by surface and bulk plasmon loss peaks. Furthermore, the primary electrons efficiency and the emission yield is modified by changes in the solid matrix.

#### 1 - INTRODUCTION

Auger electron spectroscopy (AES) is extensively used to characterize thin films materials and particularly materials surfaces. Owing to its specificity as a surface analysis technique, it allows the determination of composition profiles : the content in the different elements is followed by measuring the intensity of the Auger signal, after ionic abrasion, as a function of abrasion time.

In this work, we have tried to evaluate difficulties encountered in using that technique with three plasma deposited materials :

- amorphous hydrogenated silicon carbide  $a\text{-Si}_x\text{C}_{1-x}\text{H}$  /1/;
- amorphous hydrogenated silicon nitride  $a\text{-SiN}_x\text{H}$  /2/;
- crystallized hydrogenated aluminium nitride  $\text{Al}_x\text{N}_y\text{H}$  /3/.

## 2 - EXPERIMENTAL DETAILS

Acquisition of Auger spectra is performed with a Riber Mac2 spectrometer. It works under ultravacuum, with an incident electron beam diameter of 100 nm. Low and high energy analyses are carried out with a primary beam of 3 and 5 keV respectively. Spectra acquisition is performed in N(E) mode. The spectrometer resolution is kept at 1 eV for the analysis range 0-550 eV and at 2 eV for the range 1300-1650 eV (Si KL<sub>23</sub>L<sub>23</sub> and Al KL<sub>23</sub>L<sub>23</sub>). For particular calculations, derivative peaks  $dE.N(E)/dE$  have been used. This allows an amplification of the peaks and cancelling of the background contribution. Information being only related to the first monolayers of material, it is necessary to perform a representative analysis to eliminate the contamination layer (various contaminants, native oxide). Samples have been submitted for ten minutes to a bombardment with argon ions under an accelerator voltage of 3 kV.

## 3 - RESULTS

The composition in main elements (Al/N, Si/C and Si/N) was first determined by calculating the peak/background (P/B) ratio. The background is evaluated at the base of the peak by a linear regression from the higher energy side (Fig. 1).

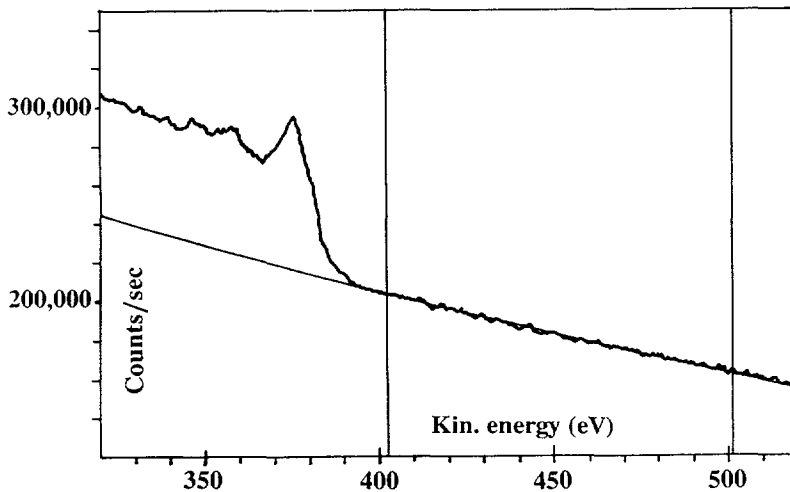


Fig. 1 - Evaluation of the primary and secondary electron background at the base of the peak by a linear regression from the higher energy side.

In a second method, peak area/background (A/B) calculations were used. After subtraction, the spectrum is relieved of the primary and secondary electron background. Then a Shirley subtraction of the background of energy loss Auger electrons and a peak fitting (gaussian deconvolution) leads to a final peak (Fig. 2) whose area is measured.

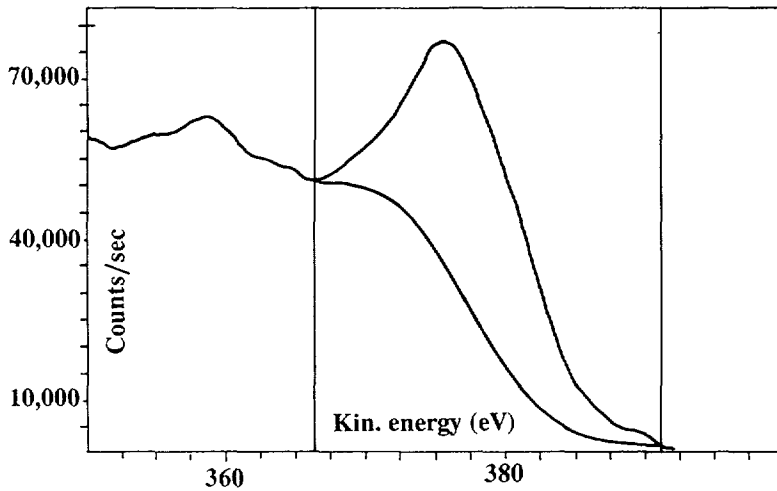


Fig. 2 - Shirley subtraction of the background of energy loss Auger electrons.

### 3.1 - a-Si<sub>x</sub>C<sub>1-x</sub>.H layers

The composition  $x$  of a-Si<sub>x</sub>C<sub>1-x</sub>.H films has been determined using a sample of epitaxial SiC as reference. This choice supposes that matrix effects in a-Si<sub>x</sub>C<sub>1-x</sub>.H films are closer to those existing in SiC than those existing in a-C:H or a-Si:H.  $x$  must not be too close to 0 or 1. The formula for determining  $x$  is used with a single "central" reference rather than two extreme references. It becomes :

$$x_{Si} = [I_{Si}/I_{Si}ref]/[I_{Si}/I_{Si}ref + I_C/I_{C}ref].$$

$I_{Si}$ ,  $I_C$  and  $I_{Si}ref$ ,  $I_{C}ref$  are peak intensities of silicon and carbon, measured respectively for analyzed films and for the reference sample. Intensities have been determined from the height of derivative peaks  $dE.N(E)/dE$  SiLVV and CKVV, from Peak/Background ratios and Area/Background ratios of SiKLL and CKVV peaks on  $N(E)$  spectra. Results are summarized in table 1.

Table 1 - Composition  $x$  (+/- 0.01) of the a-Si<sub>x</sub>C<sub>1-x</sub>.H films determined from derivative peaks  $dN(E)/dE$ , peak height  $N(E)$  P/B and peak area  $N(E)$  A/B.  $g = QSiH_4/(QSiH_4 + QCH_4)$  is the reactant flow gas ratio.

$g$	0.17	0.33	0.5
$dN(E)/dE$	0.29	0.48	0.69
$N(E)$ P/B	0.27	0.46	0.69
$N(E)$ A/B	0.24	0.49	0.69

P/B and A/B data are not very different for materials near to stoichiometry or rich in silicon because the peak of silicon is scarcely affected by the two types of bonds Si-Si and Si-C which

appear for this composition. On the other hand, P/B and A/B values are different for carbon-rich materials because the form of the peak of carbon diverges from that of the SiC reference peak and is similar to the amorphous carbon peak shape (fig. 3).

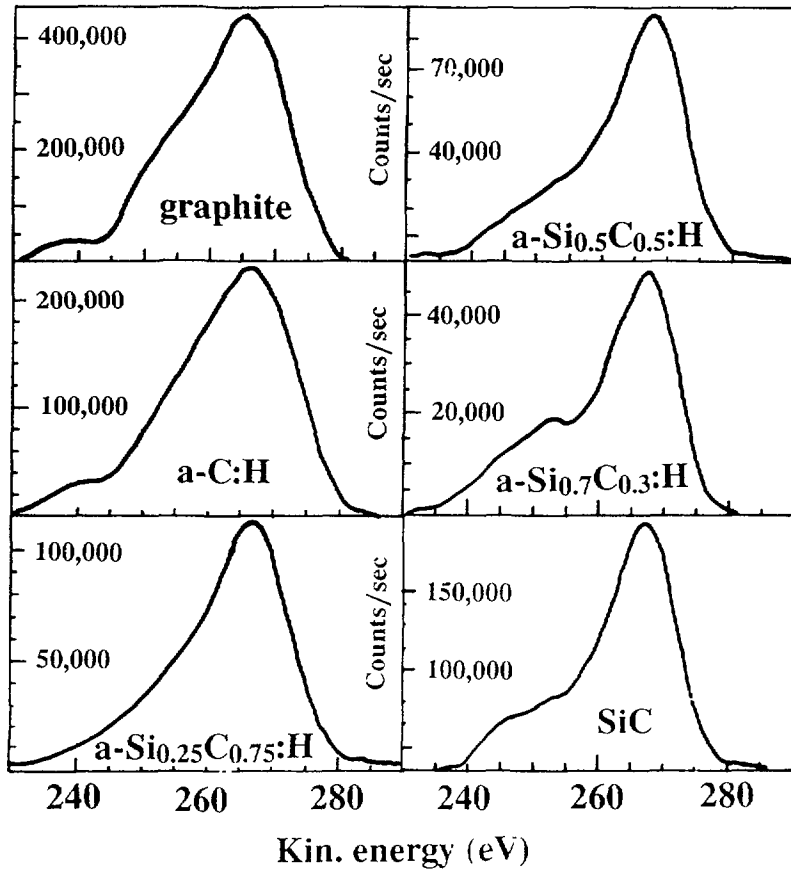


Fig. 3 - Shape modification with  $x$  of the CKVV peak compared with reference materials  $\beta$ -SiC, a-C:H and graphite.

### 3.2 - a-SiN<sub>x</sub>:H layers

Calculations of nitrogen to silicon ratio have been performed on a-SiN<sub>x</sub>:H from P/B and A/B data, using several samples of crystallized Si<sub>3</sub>N<sub>4</sub> (thermal CVD deposited layers as the "central" reference). Results are reported in Table 2.

A divergence between results from P/B and from A/B is observed. This can be attributed to the broadening effects seen on both LVV and KLL peaks of silicon. Peaks are narrow for nitrogen-rich materials and broader for silicon-rich materials indicating a multiplicity of bonds

around silicon atoms. At the same time a shift towards low kinetic energy is noticed for nitrogen-rich materials. A deconvolution in three components of the KLL silicon peak has been realized on sample 2 (fig. 4) in order to verify the bonding around silicon atoms : the two extreme peaks, about 6 eV apart, are assigned to the Si-N and the Si-Si (merged with Si-H) components; the intermediate peak represents the complex and statistically disordered environment of silicon atoms.

Table 2 - Comparison of x values calculated from Peak/Background ratio and from Area/Background ratio.  $R = Q_{\text{NH}_3}/Q_{\text{SiH}_4}$  is the reactant flow gas ratio. A light loss in nitrogen can be expected, due to ion beam damage at the surface of the sample.

Sample	R	P/B <sub>N</sub> +/- 0.02	P/B <sub>Si</sub> +/- 0.01	x = N/Si	A/B <sub>N</sub>	A/B <sub>Si</sub>	x = N/Si
1	0.5	0.25	0.11	0.91	1.60	0.53	0.78
2	0.8	0.38	0.146	1.04	2.22	0.66	0.86
3	1	0.39	0.144	1.08	2.25	0.47	1.23
4	2	0.41	0.14	1.17	2.39	0.39	1.57
5	4	0.53	0.16	1.32	3.15	0.53	1.53
Si <sub>3</sub> N <sub>4</sub>		0.50	0.15	1.33	2.70	0.52	1.33

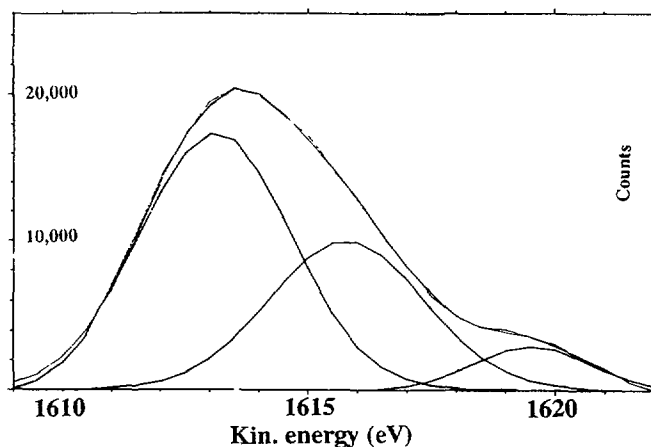


Fig. 4 - Fitting in gaussian components of the SiKLL peak for the sample 2.

Since the purpose of this paper being to highlight the difficulties encountered in using AES for quantitative analyses and not to explain the results, the explanations will be published elsewhere. That requires IR studies to determine the amount of N-H and Si-H bonds in each sample.

Numerous reference samples of  $\text{Si}_3\text{N}_4$  has been used for the determination of P/B for N and Si. The values used for  $x$  calculations (respectively 0.50 and 0.15) are those most often found for samples of good purity. Extreme values of 0.55 and 0.57 were encountered for N in thermal CVD layers obtained from organic precursors of silicon which result in carbon impurities in the material.

### 3.3 - $\text{Al}_x\text{N}_y\text{H}$ layers

The most important problem in  $\text{Al}_x\text{N}_y$  thin film quantitative Auger analysis concerns reference samples. AlN in bulk form is not suitable, because of its insulating character. Moreover, it is not available in single crystal form but only in sintered material. We used pure aluminium and  $\text{Si}_3\text{N}_4$  samples as "extreme" references. The results of P/B measurements on reference samples and on aluminium nitride layers prepared by using various deposition parameters (three different excitation frequencies, 35 kHz, 440 kHz and 13.56 MHz) are reported in table 3. Very close values of P/B are obtained for Al as well as for N. The composition of aluminium nitride layers is evaluated from P/B and theoretical density of reference compounds. The results are near to stoichiometry.

Table 3 - Estimation of composition in the aluminium nitride layers /3/.

Samples	P/B <sub>N</sub>	P/B <sub>Al</sub>	C <sub>N</sub>	C <sub>Al</sub>	C <sub>N</sub> /C <sub>Al</sub>
			mole/cm <sup>3</sup>		
References					
$\text{Si}_3\text{N}_4$	0.50		0.089		
pure Al		0.32		0.1	
Aluminium nitride					
35 kHz	0.43	0.24	0.077	0.075	1.03
440 kHz	0.45	0.25	0.080	0.078	1.03
13.56 MHz	0.47	0.26	0.084	0.081	1.04

#### 3.3.1 - Multielectronic phenomenon

The use of aluminium as reference material is one of the causes of errors. The Al KLL Auger spectrum is characterized by surface and bulk plasmon loss peaks (marked S and B respectively on figure 5) which are not found in the AlN layer spectrum. Indeed, this interaction mode has an important place in conductor and semiconductor materials. Energy losses of emitted Auger electrons occur by collective oscillations of conduction electrons. They appear as energy loss peaks inducing errors on P/B value of the principal Al KLL peak.

### 3.3.2 - Matrix effects

The Al KLL peak of pure aluminium is high and sharp (figure 5a). It appears broader and shifted in the spectrum of the aluminium nitride layer (figure 5b). A specific distribution of electronic levels corresponds to each bond type (Al-Al or Al-N). The data defined for a pure element are modified owing to the chemical bonding of this element in a material. Nevertheless, these effects are weak for core transitions. Furthermore, the primary electron efficiency and the emission yield are modified by the solid matrix changes.

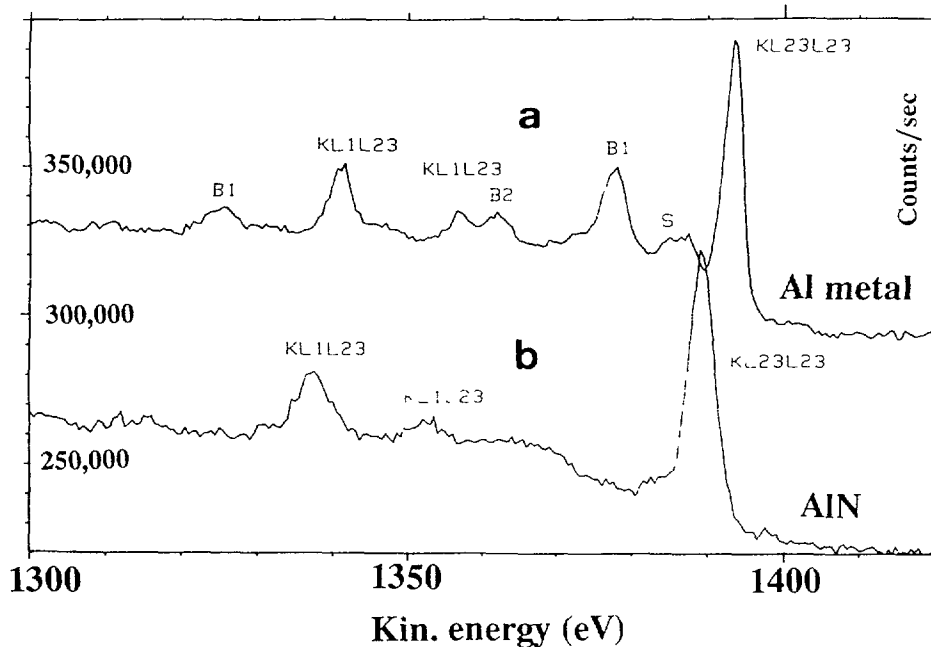


Fig. 5 - (a) Surface (S) and bulk (B1 and B2) electron-excited plasmon loss in the reference conductor material (pure aluminium). (b) Modifications induced by the chemical bonding Al-N on the Al KLL peak : shift and broadening.

## 4 - DISCUSSION

As in analyses of  $a\text{-Si}_x\text{C}_{1-x}$  and  $a\text{-SiN}_x\text{:H}$  layers, it is better to use a binary reference sample with a local structure close to the analysed sample one. When this reference is not available, as for AlN, errors due to matrix effects could be expected. In fact, the analysis on samples prepared in different conditions (varying the rf frequency), give results in good agreement (close to stoichiometry) for the composition. We can conclude that there is a compensation of the effects mentioned and consequently estimate the accuracy of AES for these analyses.



Estimation of Auger peaks is another source of errors. For a long time, derivative peaks having the advantage of virtually cancelling the background have been used. The intensity of the peak is then assimilated to the peak height at the high energy side. This method is easy to use and contributed to the success of Auger spectrometry. It is meanwhile open to criticism, because it leads to important errors when peaks shape changes or when the background is not linear (low energy peaks). Theoretically, only the measure of the area of the integrated peak is representative of the Auger transition. However, significant errors can be introduced by extrapolation of the background (Shirley method /4/). The height of the peaks is more often used, but can also lead to errors if peak shape changes. In both cases, transmission and beam current effects are avoided by using the Peak to Background ratio /5/. This is essential for comparing spectra recorded with the same apparatus in similar conditions (resolution and primary energy) and performing reliable semi-quantitative analyses.

## **5 - CONCLUSION**

In disordered materials like  $a\text{-Si}_x\text{C}_{1-x}\text{H}$  and particularly  $a\text{-SiN}_x\text{:H}$ , elements forming the structure present several types of bonds and corresponding peaks are broader than in crystallized materials. Peak height is affected by the existence of different kinds of bonds and by broadening (the deconvolution of a broad peak allows one to show the existence of several types of bonds and to evaluate statistical importance of each of them). In that case, estimation of composition from A/B ratio is more accurate than from P/B ratio.

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