Effective approaches for realizing quantitative analyses and high lateral resolution images on highly insulating samples by Auger electron spectroscopy

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ABSTRACT

The analysis of insulating materials by Auger electron spectroscopy (AES) remains difficult to achieve because of the accumulation of charges in the sample. Residual charges trapped in the specimen can lead to numerous spectra modifications such as an energy shift of the Auger transitions, enlargement, splitting and deformation of the peaks, intense or lack of secondary and Auger electrons emission.

Among the different approaches already developed to circumvent this issue, two of them were considered in this study to carry out AES experiments on a SiAlON insulating ceramic: the charge compensation method and the thin film method. For both of these methods, a systematic approach was used, combining a specific sample preparation with optimized analytical settings to mitigate the charge effects to enable quantitative analysis and high lateral resolution images.

The charge compensation method, dedicated to bulk samples, is based on the control of the total secondary electron yield (TSEY) during analysis by optimizing the intensity, the energy and the incident angle of the primary electron beam. Its combination with the metallization of the surface sample and the use of low energy Ar^+ ions to compensate the charges allowed the determination of the elemental composition of the three sub-micrometric phases of the ceramic. High lateral resolution (70 nm) Auger maps were also acquired, demonstrating therefore the long-time stability of the surface charge during acquisitions even for small analysis areas. A second method, consisting in thinning the sample down to less than a hundred of nanometres and analyzing it with a high energy electron beam, was implemented too. The results (quantification and imaging) are in good agreement with the analysis of the sample as a bulk.

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1. Introduction

Due to the rapid progress in downscaling, many materials with a wide range of applications became very important industrial and economic stakes. Thus, recent researches concern the study of material such as ceramics, VLSI devices, polymers, glasses or optical fibres. All these materials belong to the class of highly insulating specimens and, for a long time, electron spectroscopy techniques (i.e. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), reflection electron energy loss spectroscopy (REELS)) were considered to be not applicable to electrically non-conductive sample structures. Indeed, in order to analyze their surface, the specimens are irradiated with X-rays or electrons, resulting in the emission of electrons that are then collected and counted. During this process, the previous samples are subjected to charging effects because of their insulating nature.

However these analytical techniques are extremely surface sensitive and provide useful elementary, quantitative and chemical information for all elements except hydrogen and helium. Because, in XPS, the sample is irradiated with neutral X-rays, it is often possible, by using a flood electron gun if necessary, to carry out experiments in quite an easier way than for spectroscopies using a primary electron gun which contributes to the charge built up as in AES for instance. That is why XPS is one of the first techniques applied to analyze and to obtain chemical information on insulating samples, this subject being well documented [1–4]. The recent improvement of the size of the X-ray spot can be satisfactory for many problems on flat, homogeneous samples or of laterally uniform composition. However, one of the unique advantages of AES is its capability of providing compositional information with a high spatial resolution. Whereas the scale of the smallest X-ray beam in XPS is several micrometres, the nanometre scale has already been reached in AES.

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With the increasing need to analyze insulating samples at small scales, new methods or approaches allowing AES experiments, need to be developed. Indeed, charging is known to be a major obstacle in Auger for the characterization of insulating materials. The main problems generally encountered are:

- a high charge accumulation on the surface leading to the emission of intense secondary electron peaks with the release of excessive negative charges (for surfaces negatively charged) or on the contrary, the lack of electron emission outside the sample (for surfaces positively charged);
- the peaks broadening, splitting and energy shifting making more complicated or even impossible the identification of the species and their chemical state;
- the sample modification with surface and bulk damaged by the charge accumulation or maybe even the reaction of the surface [5,6];
- a non-homogeneous spatial distribution of the charge accumulation or non-constant in time.

To reduce these effects that affect AES imaging and spectroscopy, it is necessary to avoid or at least to limit charge build-up by suitable experimental analysis conditions and by specific sample elaboration and preparation. Reports on the existing methods and their ease of application have already been published and are a good starting point [7,8]. Analyzing insulators is never straightforward, especially with rough surfaces [9] and each sample requires optimized preparation and analytical conditions. The charging effects in Auger result from the low diffusion of charges both on the surface and in the specimen bulk. Samples with a low resistivity behave as resistors and lead to an energy shift of the Auger spectra, on the other hand, highly resistive specimens can be modelled as capacitors. The residual charge on the sample is then expressed as:

$$Q_s = Q_i - (Q_o + Q_d) \qquad (1)$$

where Q_s is the sample residual charge, Q_i is the incident charge, Q_o is the outgoing charge and Q_d is the diffusion charge.

This charge accumulation leads to an uneven distribution of charges across the surface and to differential charging, which strongly alters the kinetic energy and the direction of the escaping electrons. Although most of the time insulators are negatively charged due to the implantation of electrons from the primary electron beam during the analysis, they can also be positively charged: the key parameter being the total secondary electron yield (TSEY) σ defined as the ratio of the number of leaving electrons on the number of incident electrons:

$$\sigma = \frac{I_o}{I_i} = 1 - \left(\frac{I_t}{I_i}\right) \quad \text{with } I_t = I_i - I_o \qquad (2)$$

where I_i is the incident electrons current, I_o the current of outgoing electrons (i.e. secondary, backscattered and Auger electrons), and I_t the total current.

As described elsewhere [10,11] the TSEY depends mainly on the angle (θ), the energy (E) of the primary electron beam and the materials. When $\sigma < 1$ the surface is negatively charged whereas it will be positively charged if $\sigma > 1$. Most interesting are the cases when σ is equal to the unity (for a given σ a maximum of two energies E_1 and E_2 ($E_1 < E_2$) allow to achieve this). The incident electron current is then equal to the outgoing electron one and no charge should build up. This model clearly highlights the main parameters controlling the charge effects; however, it assumes a homogeneous lateral and in-depth distribution of the charges which does not correspond to an insulator submitted to an electron beam during AES analysis. The dependence of the TSEY with θ and E was recently discussed in details for insulators continuously irradiated by electrons and in terms of time evolution and depth distribution of the charge [12–14]. The TSEY varies faster with time when the surface is negatively charged. Thus, analytical conditions to obtain a slightly positively charged surface have to be favoured to perform reliable AES characterizations. Furthermore, a low positive charge at the surface of the sample will re-attract the low-energy outgoing secondary electrons that can help for charge stabilization. Moreover, the penetration depth of the primary electrons has to be in the range of the maximum escape depth of the electrons to facilitate the hole – electrons recombination's and to avoid the creation of a dipole in the sample constituted with a positively charged surface and an excess of negative charges in the bulk [12].

The purpose of this paper is to illustrate two of the common methods used to carry out AES experiments on insulating samples: the charge compensation method applied for samples in the form of bulk and the thin film method. They were applied to characterize a non-conductive SiAlON ceramic specimen. Many works dealing with the characterization of SiAlON with AES can be found in literature [15–21], but rarely with high lateral resolution. The results and the ease of their implementation will be commented.

SiAlON are ceramics mainly used as hard cutting tools, in foundries as refractory compounds but they were also recently used for the design of new LED devices. They are commonly obtained by the sintering of Si_3N_4 and Al_2O_3 powders at high temperature, the addition of a sintering additive such as Yb_2O_3 resulting in a denser material. The SiAlON adopt the crystalline structures of Si_3N_4 with the substitution of nitrogen atoms by oxygen ones in the anionic lattice whereas silicon atoms are replaced with aluminium ones in the cationic lattice. The resulting material is thus composed of sub-micronic phases: α-SiAlON, β-SiAlON and a refractory inter-granular glass. Controlling the substitution yield between anions and cations in the different phases as well as the proportion of these phases in the ceramics is of prime interest to confer a wide range of variable physical or chemical properties to these materials such as high strength, toughness, high hardness, high temperature corrosion and oxidation resistivity or low thermal expansion. The optimization of the synthesis condition requires the determination of the anions/cations substitution rate and thus the elemental quantification of the sub-micronic insulating phases.

2. Experimental

SiAlON samples with identical nominal composition were prepared, as well as reference samples (Si_3N_4 bulk, Al_2O_3 bulk and Yb_2O_3 powders) to accurately determine the relative sensitivity factors of these elements in the specific analytical condition used in this study. These samples were prepared in two different ways, depending on the characterization method used: the charge compensation method and the thin film method.

The charge compensation method was applied to bulk SiAlON, Si_3N_4 and Al_2O_3 specimens, whose surface was first mechanically polished using 3 and 0.25 μm diamond paste and sonicated in ethanol. The Yb_2O_3 powders were pressed into a pellet in order to have a flat and rather smooth surface, similar to a bulk sample. Afterwards, all the specimens were metallized with a 10 nm gold film in order to increase the diffusion of the charges and improve the homogeneity of their distribution on the surface during the AES analyses. As the escape depth of the studied Auger electrons does not exceed a few nanometres, this coating strongly attenuates the intensity of their signal. The surface was then gently sputtered in situ with an Ar^+ bombardment (1 kV, 500 nA, 1 mm × 1 mm) before the AES analysis to open an analytical window by locally removing the gold film.

For the thin film method, the preparation was similar to the production of TEM samples. The Yb_2O_3 powders were sonicated in ethanol for 15 min and a drop was deposited on a honeycomb