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► To cite this version:

G. Blondiaux, J. Debrun. Nuclear analytical techniques and applications to materials processing. Journal de Physique IV Proceedings, 1993, 03 (C7), pp.C7-2159-C7-2163. 10.1051/jp4:19937343 . jpa-00251991

HAL Id: jpa-00251991

<https://hal.science/jpa-00251991>

Submitted on 1 Jan 1993

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Nuclear analytical techniques and applications to materials processing

G. BLONDIAUX and J.L. DEBRUN

CNRS, CERI, 3a rue de la Férolierie, 45071 Orléans cedex 2, France

Abstract : This paper will present the application of Rutherford backscattering spectrometry to thin film stoichiometry determination and application to optimization of the film process elaboration in the case of dielectric films (Ge,Pb,O) and ionic conductors films (Na,Al,O). After we shall present the application of particles induced gamma emission (PIGE) for the characterization of ternary compounds (B,Si,C) used as coating to protect composites materials. The last part of this paper will describe the determination of oxygen in the bulk of fluoride glasses with charged particles activation analysis.

I. RBS contribution in the elaboration and optimisation of thin amorphous films.

Since several years a lot of work is done in the field of thin films elaboration [1,2]. Among them, dielectric (Ge,Pb,O) and ionic conductors (Na,Al,O) are studied for their application in microelectronic devices. To optimise an elaboration process, we must be able to determine composition of the deposit as a function of elaboration parameters.

After elaboration we have use Rutherford backscattering spectrometry (RBS) to characterize these thin films ; this allow us to determine Na/Al and Ge/Pb ratios and also oxygen concentration. All these techniques are utilised to study the different parameters bounded to the elaboration process.

Nuclear analytical technique.

Determination of thin films composition and moreover the stoichiometry is not easy to solve with conventional analytical techniques. Rutherford backscattering spectrometry is one of the most powerfull method for the analysis of thin films [3]. For light element RBS has a very good resolution in term of mass, but substrate must be of lower atomic number than the components of the deposit. The number of count versus the energy of the backscattered particles give information on the composition and the thickness of the film allowing us to determine stoichiometry.

In this application we have use a 2 MeV alpha beam from the single ended Van de Graaff at CERI, particles were detected at 160° with a 25 mm² detector at a distance of 100 mm, beam current was in the range of 10 to 50 nA. Thin films to be analysed were deposited on vitreous carbone. We have measured Na/Al, Ge/Pb ratio and oxygen concentration. Figure 1 show a typical spectrum obtained on Na-Al-O thin film.

Results and discussion.

We have studied several parameter of the elaboration process : initial vacuum, target composition, RF power, plasma pressure and composition. The initial vacuum must be lower than 10⁻³ Pa to get stable films ; RF magnetron sputtering technique must be used to limit the alkali loss. Plasma pressure must be close of 0.5 Pa to minimize argon incorporation and to get homogeneous composition. The most interesting results obtained by RBS

analysis is the fact that the films compositions are directly dependent of the combination. RF power and plasma composition. Figures 2 display some results obtained with RBS analysis.

In conclusion RBS allow quick determination of thin films stoichiometry and a rapid optimization of the elaboration process.

II. Analysis of ternary compounds (B+C+Si) and application to the optimization of a C.V.D. process.

Composites materials (C/C or C/SiC) are of great interest in the manufacturing of spacecraft because of there excellent mechanicals properties at high temperature, but they have a rather poor resistance to oxidation. Coating made out of ternary compounds (B+C+Si) of appropriate composition can provide protection. These coating can be obtained by C.V.D. The growing process of such layers depend of various parameters. Because theoretical calculations are only indicative and to have a good control and optimization of the process, it is very important to analyse qualitatively and quantitatively these coatings. One must say that there is a lack of accurate methods to determine the composition of thin B+C+Si layers. Nuclear methods are very powerfull for the determination of light elements [5] and we have developped a method based on (p,p' γ) reactions on ^{10}B and ^{28}Si at 3.1 MeV.

Boron is determined with the following reaction : $^{10}\text{B}(p,p'\gamma)^{10}\text{B}$
The energy of the incident proton beam is 3.1 MeV. The gamma at 718 KeV is measured with a high purity germanium detector (FWHM : 1.8 KeV efficiency : 15%) ; detection is at 90 degrees of the incident ions beam .

For silicon we use (p,p' γ) reaction on ^{28}Si : $^{28}\text{Si}(p,p'\gamma)^{28}\text{Si}$
For this determination the 1778 KeV gamma ray is used. Samples for standardization are made of pure boron and silicon targets.

Carbon determination.

Carbon determination was not possible during boron and silicon analysis ; we have just checked that the determination by difference was accurate. Only hydrogene and chlorine deposits could occur, but thermodynamical calculation have shown that this hypothesis is highly improbable For this purpose activation analysis with the $^{12}\text{C}(d,n)^{13}\text{N}$ reaction is used.

Results and discussion.

Different kind of samples were analysed in order to compare thermodynamical studies with experiments. The composition of the deposits vary with the composition of the gaseous phase (H_2 , BCl_3 , CH_3SiCl_3) which is changed through the following ratios between the inlet concentrations :

$$\alpha = [\text{H}_2]/[\text{CH}_3\text{SiCl}_3] \quad \beta = [\text{CH}_3\text{SiCl}_3]/[\text{BCl}_3]$$

Studies have been done for a temperature of 1400 K and a pressure of 0.395 atm, a mass flow rate of 0.320 g/min and a fixed α ratio of 10, 20, 40. Figure 3 give an example of the results obtained. From these results it seems that for $\alpha = 20$ boron concentration is slightly different from the thermodynamical calculations specially for $\beta = 1$. For $\alpha = 10$ and β varying there is a difference from the predictions for silicon concentrations, probably because a low hydrogen concentration did not facilitate silanes reduction.

We have also checked thickness and chemical composition uniformities ; figure 4 give an example of the results obtained.

With this work, we have shown that nuclear analytical techniques can be very usefull to solve the problem of light element determination. In that case PIGE is a rapid method, easy to use allowing the analysis of a large number of samples which is necessary for the optimization of a C.V.D process.

III. Fast analysis of oxygen in fluoride glasses by charged particles activation.

Fluoride glasses have very low losses and were proposed for the making of ultra-low loss optical fibers [6]. Extrinsic losses are due to absorption by mettalic ions and by hydroxyl groups and to scattering due to bubbles crystallites or oxydes. It has been shown that the higher the total oxygen contents, the higher the losses by scattering.[7]. To determine oxygen concentration in these glasses we propose a method which is fast and only requires the use of a small accelerator.

Experimental method.

We use radioactivation via the $^{16}\text{O}(\text{d},\text{n})^{17}\text{F}$ reaction. ^{17}F is a pure β^+ emitter of 66 s of half life. After a 3 min irradiation with 2.8 MeV deuterons, we do etching of 6-8 μm to remove surface contamination. Pure alumina is used as standard. Gamma spectrometry is done on the 511 KeV peak and the decay is checked in all cases.

Results.

At this level the analysis is completed in about 15 min and the overall precision is 15 %. Concentrations in the glasses were found to range from 200 up to 500 ppm/weight.

As the purity of the glasses improves, other method may be needed, because the present method will not be sufficiently sensitive. Activation will probably remain a method of interest at lower levels because it is possible to eliminate surface contaminations. The best way to improve the sensitivity of the activation technique is to use tritons particles. The $^{16}\text{O}(\text{t},\text{n})^{18}\text{F}$ reaction is selective for $E < 4$ MeV and has a high cross section at low energy. For instance the sensitivity is 0.05 ppm/weight at 3 MeV for an irradiation of 10 min at 100 na[8].

IV. Conclusion.

In this paper we have described three applications of nuclear techniques used to solve problems of characterization of new materials. These analytical methods which are fast and easy to use are especially interesting in the case of light elements determination.

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Figure 1 : RBS spectrum showing the influence of initial vacuum before sputtering process on Na-Al-O thin film.

Figure 2 : RBS results showing the sodium content in the films related to oxygen percentage in the plasma (RF power : 70w, pressure : 0.5 Pa ; target-substrate distance : 90mm).

Figure 3 : Comparison between the thermodynamical calculations and the experiments at $\alpha=20$, β variable, $T=1400\text{K}$, $P=0.395\text{ atm}$.

solid line : thermodynamic.

dashed line : experiment.

■ $\diamond$: boron. ● ○ : silicon. ▲ $\triangle$ carbon

Figure 4 : thickness and chemical composition (in at %) uniformities at 1400 k , $p=0.395\text{ atm}$, $\beta=1$, 0.320 g/min .