

Simultaneous quantification of light elements in thin films deposited on Si substrates using proton EBS (Elastic Backscattering Spectroscopy).

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Abstract

Quantification of light elements content in thin films is an important and difficult issue in many technological fields such as polymeric functional thin films, organic thin film devices, biomaterials, and doped semiconducting structures.

Light elements are difficult to detect with techniques based on X-ray emission, such as energy dispersive analysis of X-rays (EDAX). Other techniques, like X-ray photoelectron spectroscopy (XPS), can easily quantify the content of light elements within a surface but often these surface measurements are not representative of the light elements global composition of the thin film. Standard Rutherford backscattering spectroscopy (RBS), using alpha particles as probe projectiles, is not a good option to measure light elements deposited on heavier substrates composed of heavier elements like Si or glass. Nuclear Reaction Analysis (NRA) offers a good quantification method, but most of the nuclear reactions used are selective for the quantification of only one element, so several reactions and analysis are necessary to measure different elements.

In this study, Elastic Backscattering Spectroscopy (EBS) using proton beams of 2.0 MeV simultaneously quantified different light elements (helium, carbon, nitrogen, oxygen, and fluorine) contained in thin films supported on silicon substrates. The capabilities of the proposed quantification method are illustrated with examples of the analysis for a series of thin film samples: amorphous silicon with helium bubbles, fluorinated silica, fluorinated diamond-like carbon and organic thin films. It is shown that this simple and versatile procedure allows the

simultaneous quantification of light elements in thin films with thicknesses in the 200–500 nm range and contents lower than 10 at. %.

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1. Introduction

Quantification of light elements content in thin films is an important and difficult issue in many technological fields. For example, polymeric thin films functionality depends on the composition of the light elements carbon, nitrogen, and oxygen [1]. Helium implantation in silicon has been generated for studies of the properties of the voids it creates [2, 3] and the relation between these voids and optical properties [4]. Precise knowledge of the F content is an important issue in coatings with antiseptic functionality based on fluorinated carbon films (CF_x), where a correlation between hydrophobicity and bacterial anti-adherence performance with their F content has been reported [5]. The quantification of this element is also important in low refractive index films and low k interlayer dielectrics [6, 7] based on fluorinated silica films (SiOF) [8,9].

Despite of the importance of the control of light elements content for the applications mentioned above, the quantification of these elements in thin films is not an easy task. They can be detected by techniques based on X-ray emission like energy-dispersive X-ray analysis (EDS), but quantification is difficult because of the self-absorption of the low energy X-rays and the broadening of the beam into the specimen [10]. Other techniques like X-ray photoelectron spectroscopy (XPS) can easily quantify the presence of light elements content within a surface, but quite often these surface measurements are not representative of the light element thin film composition [11].

Infrared spectroscopy is also often used to this aim. However, although this technique is strongly sensitive to organic bonds type formation [12], its quantitative information is more doubtful.

Helium bubbles of microscopic size have been detected in metals by absorption, electron energy loss, and fluorescence spectroscopy [13]. However, these techniques do not give quantitative information about the helium content in the bubbles. Helium content in metal thin films has already been measured by elastic backscattering using proton beams [14, 15] and bubble density in metals, has been measured by optical absorption [16] and a combination of EELS with TEM [16] or neutron scattering (SANS) [17].

Nuclear reaction analysis (NRA) by means of several reactions is also extensively used for light elements quantification purposes. In this case, specific reactions are chosen for each element and quantification relies on comparative studies with well-known reference samples. Information about quantification of helium, carbon, nitrogen, oxygen, and fluorine using NRA and other IBA techniques can be found in the literature [18-22] and references therein. A combined method to determine fluorine concentration in thin films deposited over different substrates using a combination of Rutherford backscattering spectroscopy (RBS) and particle induced gamma ray emission (PIGE) has also been described by our group [23].

Standard Rutherford backscattering spectroscopy, using alpha particles as probe projectiles, is also used to determine the light elements content in thin films. In this case, the films are quite often deposited on artificial light substrates (such as graphite) with an added (heavy element) interlayer to simplify the elemental quantification [24]. This is due to the low scattering cross section and kinematic factor for these elements that, in most cases, strongly handicaps its quantification. The choice of graphite as a substrate generally avoids the overlapping of signals from the substrate and the deposited light elements films, so that light elements quantification becomes straightforward. However, this trick is not always possible and quantification of light element content in thin films deposited in other standard substrates, such as Si wafers, is generally not an easy task.

In this work we propose Elastic Backscattering Spectroscopy (EBS) using proton beams at 2.0 MeV to determine simultaneously various light elements content in thin films deposited on silicon substrates. Even if the capabilities of EBS using proton beams have been known for more than 40 years [25], not many papers have been written about analysis using this technique in materials science. Of them, only about one dozen are devoted to bulk samples and another dozen to thin samples. For the thin films, oxygen is the element most studied [26-31], followed by nitrogen and carbon [26, 27, 32], helium [15,16], and fluorine [31]. The method proposed is of special interest for

laboratories where only proton sources are available for quantification purposes and to determine at the same time various light elements (He, C, N, O and F) content for samples deposited over silicon substrate.

2. Materials and methods

2.1. Rutherford backscattering spectroscopy

EBS characterizations were performed at the 3 MV tandem accelerator of the National Center for Accelerators (Seville, Spain). EBS beams measurements were performed with protons of 2.0 MeV and a passivated implanted planar silicon (PIPS) detector located at 165° scattering angle. This energy was chosen to avoid interferences of resonant cross sections of different elements present in the samples and to clearly separate the signals coming from the light elements (He, C, N, O and F) in the measured spectra.

Light element (LE) content was characterized by EBS using a proton beam against a reference used for standard RBS quantification. We used a sample with a well-known amount ($18 \times 10^{15} \text{at/cm}^2$) of Pt deposited over a Si substrate. This is done, in the assumption that LE content is homogeneously distributed in depth. Fitting adjustment using advanced codes like SIMNRA is not appropriate in this case due to the high porosity and microstructural morphology of the samples, that induces to artifacts in the simulation.

Samples containing Si were also measured with protons of 1.0 MeV to increase the stopping power in order to split contributions of Si coming from the film and from the substrate. In order to check the quality of the method, standard RBS with alpha particles of 2.0 MeV have also been used to characterize some of the samples.

2.2. Sample preparation

Fluorine rich amorphous carbon (CF_x) samples were obtained by simple plasma decomposition [33]. Fluorine doped silica (SiOF) thin films were prepared by reactive magnetron sputtering [34]. Amorphous Si coatings with closed porosity samples containing He and O (Si:He) were produced by magnetron sputtering [35]. Organic thin films containing C, N, O (CNO) were prepared via polymerization of dye molecules by interaction with a remote plasma [36] over polished Si substrates. At the same time, samples were deposited over vitreous carbon covered with

a Ag interlayer of 60 nm, deposited by plasma assisted vacuum deposition (PAVD). The latter samples were fabricated to analyze them by RBS with alpha particles.

3. Results

In this section we present the results of light elements quantification in three sets of samples: i) Fluorine rich amorphous carbon (CF_x) and fluorine doped silica (SiOF) thin films; ii) amorphous silicon with helium bubbles (Si:He-O); and iii) organic thin films containing C, N and O (CNO). These results illustrate the capabilities of the proposed analysis method.

3.1. CF_x and SiOF

Figure 1a) shows the EBS spectrum of one of the SiOF samples. It clearly shows three different peaks corresponding to carbon, oxygen and fluorine. In the inset of the figure, we have zoomed the region where these peaks appear and we have drawn a background line to guide the eyes. As the stopping power of 2.0 MeV protons in SiOF samples is not high enough, the thickness of the samples is not sufficient to clearly differentiate between silicon signals coming from substrate and silicon signal coming from the sample. For this reason, silicon content was calculated from EBS spectra, not shown here, with protons of 1.0 MeV. In these conditions, energy lost in these samples is bigger and both signals can be differentiated.

3.2. Si:He

Figure 1b) shows a EBS spectrum of one of the Si:He samples. An intense peak corresponding to He and the oxygen contribution can be observed over the substrate signal. In the high energy part of the spectrum of the thicker sample (Si:He-3) (not shown here) we can also see a step corresponding to the difference between Si signals coming from the porous thin film and from the substrate.

3.3. CNO

Three different peaks can be clearly observed in EBS spectra of the organic samples, Figure 1c). over the silicon signal of the substrate corresponding to carbon, nitrogen and oxygen, as indicated in the figure.

In order to verify the accuracy of the method, RBS analysis with alpha particles of 2.0 MeV was done to samples deposited over glassy carbon substrates + Ag interlayer. These spectra are shown in Figure 2. Carbon signals related to the film and to the substrate are separated because of the Ag interlayer deposited over the glassy carbon substrate that can sufficiently stop the ion beam. The atomic percent for carbon, nitrogen and oxygen content obtained by both methods (EBS and standard RBS) is represented in Figure 3. A straight line (1:1) has been drawn to guide the eyes.

Elements content of the three set of samples is shown in Table 1. Uncertainties has been calculated considering statistical and contributions due to substrate signal subtraction.

4. Discussion

Accurate elemental quantification of light elements (He, C, N, O, and F) in samples deposited on substrates composed of elements with higher atomic number is strongly handicapped by standard RBS with alpha particles. It is obvious that helium can not be detected using standard RBS with alpha particles. For the rest of the elements, the overlapping of the signals, as a result of the stopping of the alpha projectiles and the low cross section of these light elements compared with those of the substrate, are the two main reasons that standard RBS is difficult for this purpose. We can overcome this limitation using EBS. Due to the kinematic factor dependence with the target elements, protons result in a better projectile for separating different light elements in the Rutherford backscattering spectra [52]. In addition, the lower stopping power of protons, compared to alpha particles, avoids the overlapping of the signals of different light elements when the thickness of the sample is ≈ 500 nm.

Moreover, the corresponding ratio of the cross sections σ_{LE}/σ_{Si} increases about 4-5 times, except for fluorine where a little decreasing is observed (σ_C/σ_{Si} : 0.15 \rightarrow 0.87; σ_N/σ_{Si} : 0.22 \rightarrow 1.03; σ_O/σ_{Si} : 0.30 \rightarrow 1.12; σ_F/σ_{Si} : 0.39 \rightarrow 0.26) when 2.0 MeV protons are used instead of 2.0 MeV alpha particles. Evaluated (SigmaCalc) cross section data were retrieved from the IBANDL database, IAEA, 2013 [37], for He, C, N and O and from Jesus et al. [38] for F. The increase of the cross section, together with the splitting of the signals from the He, C, N, O, and F, allow straightforward elemental quantification of these light elements in the films. This is the case illustrated in Figure 1c), where

the signals from C, N, and O atoms of CNO samples are clearly separated to facilitate elemental quantification. Even if we could find better conditions at lower energy to improve the fluorine cross section [38], working at 2.0 MeV energy is also a good solution because the critical angle for channeling effect increases as the square root of the inverse of energy [39] and a distortion in the higher edge of substrate Si signal could be produced due to this effect when working at lower energy. In situations where this partial channeling condition appears, it is more difficult to define a good and constant background to distinguish C, N, O and F signals over Si substrate signal.

In order to compare EBS using proton beams with the more standard RBS with alpha particles, we have represented C, N and O content determined by both methods. In Figure 3 we can see a good agreement between both methods. In our case, this agreement is better for C, whose content is over 80 at. %. In this situation, the difference between EBS and RBS with alpha particles is less than 3 %. However, for N and O, with a much lower content, differences are bigger and can rise to 25%. This is due to the low statistic (and proximity to the LLD) for these signals and results can be improved if a higher beam dose is accumulated (better statistic).

Using our experimental conditions of measurements and considering the definition of low level of detection (LLD) as three times the root mean square of the background, an LLD of $4 \times 10^{15} \text{at/cm}^2$, $30 \times 10^{15} \text{at/cm}^2$, $25 \times 10^{15} \text{at/cm}^2$, $20 \times 10^{15} \text{at/cm}^2$ and $130 \times 10^{15} \text{at/cm}^2$ can be considered for He, C, N O and F respectively.

5. Conclusions

We have proposed a method to determine simultaneously light elements content (He, C, N, O and F) as low as 1 (± 0.3) at. % in thin films (200-500 nm thickness) deposited on silicon substrates. It consists EBS with protons with 2.0 MeV energy and a PIP Si detector at 165° . This method uses only proton beams as probe projectiles. We have shown the performance of the proposed analysis with three different series of samples (CF_x and SiOF, Si:He and CNO thin films) of technological interest containing light elements within their structure. Finally we have correlated EBS method with standard RBS with alpha particles.

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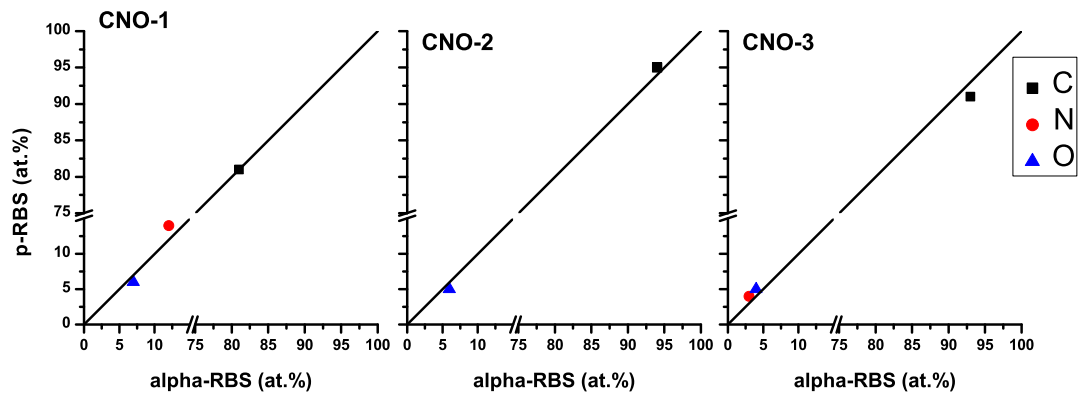


Fig.1. EBS spectra acquired with 2.0 MeV protons of sample SiOF-1, SiHe-3 and CNO-1 deposited on Si substrate.

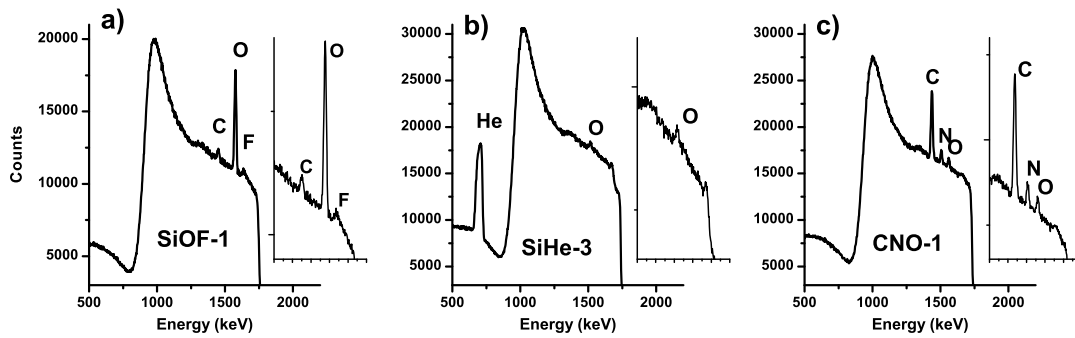


Fig.2. Standard RBS spectrum acquired with 2.0 MeV alpha particles of samples CNO-1 deposited on glassy carbon.

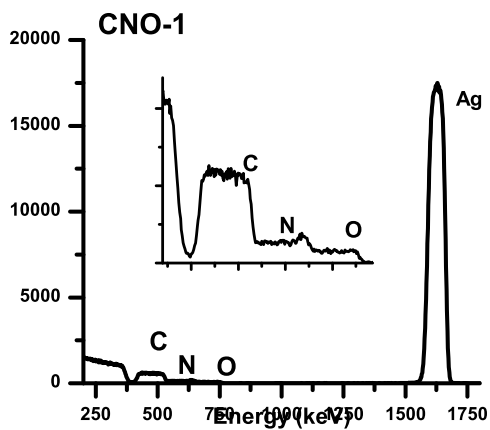


Fig.3. Carbon, nitrogen and oxygen content (at.%) obtained from EBS spectra acquired with 2.0 MeV protons versus content (at.%) obtained from alpha-RBS spectra acquired from samples CNO-1, CNO-2 and CNO-3 deposited on silicon and glassy carbon + Ag interlayer, respectively.

Sample	Si	He	C	N	O	F
	(10 ¹⁵ at/cm ²)					
CFx	--	--	313 ± 16	--	47 ± 12	528 ± 79
SiOF-1	490 ± 25	--	122 ± 6	--	978 ± 147	387 ± 77
SiOF-2	1028 ± 51	--	421 ± 21	--	2119 ± 106	469 ± 47
Si:He-1	1100 ± 55	504 ± 25	--	--	--	--
Si:He-2	1646 ± 82	501 ± 25	--	--	105 ± 16	--
Si:He-3	4600 ± 230	816 ± 41	--	--	60 ± 12	--
Si:He-4	1245 ± 62	45 ± 5	--	--	282 ± 28	--
CNO/Si-1	--	--	894 ± 45	129 ± 13	82 ± 12	--
CNO/Si-2	--	--	986 ± 49	0	66 ± 13	--
CNO/Si-3	--	--	1277 ± 64	40 ± 10	65 ± 13	--

Table 1. Elements content in CFx, SiOF, and CNO samples calculated from EBS measurements using proton beams.

Sample	Thickness (10 ¹⁵ at/cm ²)	C (at.%)	N (at.%)	O (at.%)
CNO/C-1	3300	81	14	6
CNO/C-2	2600	95	0	5
CNO/C-3	3200	91	4	5

Table 2. Elements content in CNO samples calculated from standard-RBS measurements using alpha particle beams.