Determination of the density of silicon–nitride thin films by ion-beam analytical techniques (RBS, PIXE, STIM)

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Abstract This work presents the investigation of some commercially available and commonly used Si_3N_4 foils prepared with LPCVD technique. The density and the stoichiometry of these films were determined by Rutherford backscattering spectroscopy and profilometry, while the study of impurities was achieved with particle induced X-ray emission method. It was found that the density of the studied Si_3N_4 films is significantly less (~ 2.71 g cm^{-3}), while the stoichiometry is close to the values of the bulk material. The results were verified by measuring the ion energy loss through the films by scanning transmission ion microscopy.

Keywords Silicon–nitride film · Rutherford backscattering spectroscopy (RBS) · Scanning transmission ion microscopy (STIM) · Particle induced X-ray emission (PIXE)

Introduction

Thin films of silicon nitride (SiN_x) have very attractive physical and chemical properties, such as high thermal stability, high electrical resistivity, chemical inertness, extreme hardness and good dielectric properties. Therefore, they are widely used in microelectronic devices [1] or in micromechanical sensors [2]. They can be used as electrical insulators or a diffusion barrier when they are used as a mask [3]. Furthermore, because of their high mechanical resistance the silicon–nitride thin films are commonly used as a high-vacuum window—for example in accelerator based external ion beam applications or atmospheric scanning electron microscopy—or in nuclear physics experiments as a nitrogen and silicon standard material [4–6].

These films are commonly prepared by low pressure chemical vapour deposition (LPCVD) method from a gas mixture of dichlorosilane (SiH_2Cl_2) and ammonia [7, 8]. By controlling the composition of these films it is possible to modify certain physical and electrical properties, such as refractive index, band gap, dielectric constant, density and stress, which are important for the desired applications. Although a large number of detailed investigations [9–11] have been carried out on the deposition and characterization of silicon–nitride films obtained by different preparation techniques, it is still a challenge to characterize the quality and the stoichiometry of the produced thin films. Most preparation technique claim to produce quality and stoichiometric material, while there is no experimental method which is able to verify the above properties easily. Furthermore, in many applications, beside the quality and the stoichiometry, the density of the film is also a crucial parameter (for example in nuclear physics experiments as a standard material or as a vacuum window in external particle beam setups). However, the density of the prepared silicon–nitride film is mostly unknown or it is estimated from the density of the bulk, stoichiometric Si_3N_4, which can be very far from the real density value. Previously, the density of a laboratory prepared non-stoichiometric SiN_x films on silicon substrate were investigated by different techniques [12], but it is still different from the value accepted and used nowadays (~ 3.1–3.44 g cm^{-3}) for SiN_x films prepared by LPCVD method.

In this article, we report the determination of the density of some commercially available and commonly used Si_3N_4

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foils by Rutherford backscattering spectroscopy (RBS) and profilometry technique. In order to minimize the error and to verify the obtained results scanning transmission ion microscopy (STIM) method was applied. In addition, characterization of the impurities may be present in the thin films was achieved by PIXE spectroscopy method.

Experimental details

In our investigation we analysed LPCVD deposited Si_3N_4 foils [13] with various thicknesses from two manufacturers: 100 and 200 nm thick foils from Norcada Inc. and 200 and 500 nm from Silson Ltd. The uncertainties of the Si_3N_4 foils thickness was given between 7 and 10 %, the stoichiometry of the foils is close to the ~ 0.75 Si/N. Moreover, in the absence of self-measurements the density given by the manufacturers was 3.1 g cm^{-3}.

The experiments were carried out on the Oxford-type [14] nuclear microprobe facility at the Institute for Nuclear Research, Hungarian Academy of Sciences, Debrecen, Hungary [15]. The energetic ions were produced by a 5 MV single ended Van de Graaff accelerator.

Rutherford backscattering spectrometry measurements were implemented with focussed 1000, 1500 and 1600 keV He$^+$ ion beams. Two ORTEC-type surface barrier silicon detectors ("ULTRA" ion-implanted, 50 mm^2 sensitive area and 25 keV system energy resolution) were used for the RBS measurements, simultaneously. One of the detectors was placed at a scattering angle of 165° at Cornell geometry and the other one was set to 135° at IBM geometry [16, 17]. The beam was focussed to a 2×2 μm^2 spot while the scan size was set to 500×500 μm^2. The sample chamber is equipped with a high precision vacuum generators 5-axis goniometer. Two laser beams placed at 45°–45° degrees to the ion beam was used to position the sample to the appropriate geometry.

The system accuracy was verified on palladium standards with different thicknesses (50, 100, 150, 200 nm) evaporated onto a silicon substrate. The real layer thicknesses were measured by an independent technique (profilometry). The uncertainty was determined based on the deviation between the layer thickness obtained from profilometry and measured by RBS. Thus, the measured stoichiometry and areal atomic numbers were taken into account with 3 % uncertainty.

In order to get more detailed information of the composition of the Si_3N_4 films, PIXE measurements was performed using 2000 keV H$^+$ ion beam. The experimental setup consists of two Si(Li) X-ray detectors—an ultra-thin windowed and a Be windowed one—for the simultaneous and efficient detection of light, medium and high Z-number elements [18, 19].

Scanning transmission ion microscopy experiments were carried out with 1000 and 1600 keV He$^+$ ion beam in order to verify the thickness and density of the foils, by measuring the energy loss of the ions through the foils. For these measurements, a 50 mm^2 Canberra type PIPS particle detector (11 keV nominal energy resolution) was installed at on-axis geometry, 60 mm from the sample. The measured energy loss was influenced by the energy spread of the accelerator which is around 1 keV [20].

RBS spectra were evaluated with the SimNRA computer code version 6.06 [21] and for the evaluation of the PIXE spectra the GUPIXWIN program package was used [22]. The ion energy loss was calculated with the SRIM code [23] (for the calculations the measured sample thicknesses were taken into account).

In order to determine the thickness of the silicon–nitride films a profilometer instrument was applied (AMBIOS XP-I type). The average thicknesses of the foils were determined in several points after the ion beam analytical (IBA) measurements. In order to eliminate the uncertainties from the thickness determination we ruptured the foils and we carried out the profilometry measurements at least three different points, close to the RBS and STIM measurement areas. Due to the high accuracy of the profilometer instrument (±1 nm), the main source of the uncertainty of the measured thickness is the inhomogeneity of the foils. Therefore we give an estimate of 4 % as the uncertainty of the thickness. This value was calculated from the standard deviation of the measured thicknesses of the foils with different nominal thickness. For the density calculations, the averaged thickness of each samples (foils) were used.

The final uncertainty of the density values was derived from the quadratic sum of each parameter such as stoichiometry (3 %), areal atomic number (3 %) and thickness of foils (4 %). These final uncertainties are indicated in Table 1.

Results and discussion

Rutherford backscattering measurements

The direct determination of the density of a deposited thin film is mostly impossible. However, it can be determined by measuring the thickness and the areal atomic number (atom cm^{-2}) of the film directly, for example, by IBA techniques [24]. It is known that the density of thin films is generally lower than the bulk density. The information gained from IBA measurements about film composition, film areal density and physical thickness by profilometer can be used to calculate the film density.

In our study, RBS measurements were carried out to determine the atomic number and profilometer measurements were performed to achieve the thicknesses of the Si_3N_4 films.

Table 1 The measured thickness, the measured areal atomic concentrations, the silicon–nitrogen stoichiometry and the calculated densities of the different Si_3N_4 films and their uncertainties

Sample	Measured foil thickness (nm)	Atomic areal concentration ($\times 10^{15}$ atom cm^{-2})	Stoichiometry (Si/N)	Density (g cm^{-3})
Norcada 100 nm	94 ± 4	785 ± 24	0.84 ± 0.03	2.82 ± 0.16
Norcada 200 nm	187 ± 7	1565 ± 47	0.88 ± 0.03	2.85 ± 0.17
Silson 200 nm	207 ± 8	1668 ± 50	0.77 ± 0.02	2.69 ± 0.16
Silson 500 nm	449 ± 18	3638 ± 110	0.73 ± 0.02	2.68 ± 0.16

The sample name shows the producing company and the nominal thickness

The density value of the films produced by different manufacturer show differences. Nevertheless, the density values are equal within 1 sigma uncertainty. Thus, the 2.71 ± 0.11 g cm^{-3} value is accepted as an average density value and standard deviation of these foils, which was calculated taking into account each measurements
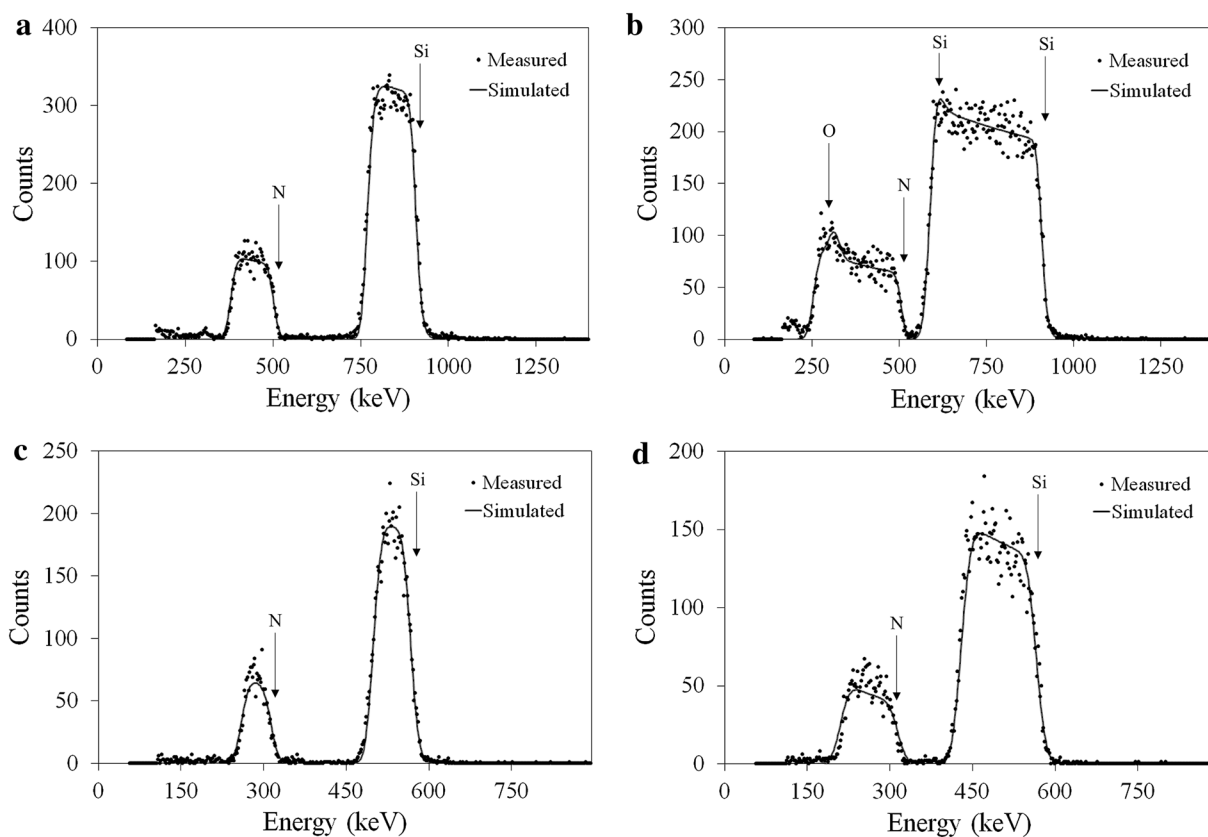

Fig. 1 RBS spectra of **a** Silson 200 nm **b** Silson 500 nm thick Si_3N_4 (irradiating ions: 1.6 MeV He^+) and **c** Norcada 100 nm and **d** Norcada 200 nm thick foils (irradiating ions: 1.0 MeV He^+). The measured data was fitted and the spectra were simulated with the SimNRA code.

In the case of the sample Silson 500 nm (**b**), a new silicon-oxide layer had to be introduced into the backside as a second layer for a good fit (because of that, the O peak of the SiO_2 shifted to the lower energies)

Figure 1 shows the RBS spectra recorded on Si_3N_4 foils with various thickness.

In the case of the 500 nm thick samples, the simulated spectra did not fit well with the measured data if only silicon–nitride layer was taken into account. Significant N shift was observed in the Si/N stoichiometry. A new silicon-oxide layer (about 2×10^{17} atom cm^{-2}) had to be introduced into the backside as a second layer for a good fit (its peaks can be seen on Fig. 1b). Independently from this, oxygen impurities may be exist in the film homogeneously. The presence of oxygen in the layer suggests that oxidation of the silicon might happened. This oxide layer might occur during the production, since the fabrication of thicker layers is not a one step process, so between the production steps oxygen may be built into the layers as silicon-oxides. Oxygen was detected by the PIXE measurements as well (see next chapter).

The result of the fitting procedure, the atomic number per unit area (atom cm^{-2}) was obtained which was converted to g cm^{-2} first and then it was divided by the thickness.

Table 1 shows the average thickness, the measured areal atomic concentrations and the calculated densities of the different Si$_3$N$_4$ films.

STIM analysis

Scanning transmission ion microscopy measurements were performed with 1000 and 1600 keV He$^+$ ion beam in order to verify the thickness and density of the foils. We measured the energy loss of the ions passing through the foils and compared it with the calculated energy loss values using the SRIM code with the built in density ($\sim$3.44 g cm^{-3}) and our determined densities of the Si$_3$N$_4$. Figure 2 shows the spectra of the STIM measurements recorded on Norcada 100 nm and Norcada 200 nm Si$_3$N$_4$ foils using 1.0 MeV He$^+$ ion beam.
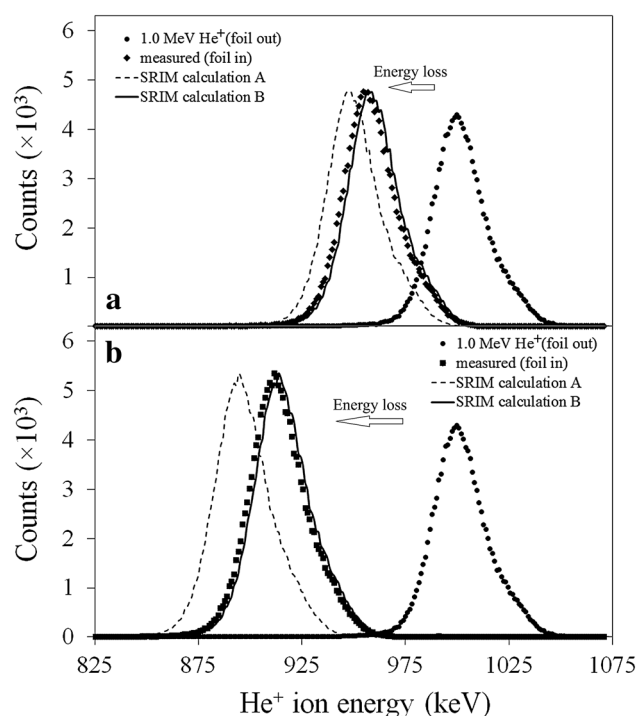

Fig. 2 The STIM spectra of **a** Norcada 100 nm (*filled diamond*) and **b** Norcada 200 nm (*filled square*) Si$_3$N$_4$ foils using 1.0 MeV He$^+$ ion beam (*filled circle*). The SRIM calculation A was performed using the built in density value ($\sim$3.44 g cm^{-3}) of the Si$_3$N$_4$ (*dashed line*), while in the case of SRIM calculation B we used the density values which were determined in this work (*straight line*, see Table 1). The measured curve is shifted with the calculated energy loss to visualise the calculated data (for the calculations, the measured sample thickness was used). The energy spread and the determination of central position of peaks may cause 3 % uncertainty in the values of the energy loss

The calculated He$^+$ energy losses through the Si$_3$N$_4$ films fit very well with the experimental results when the densities determined by the RBS method were used. However, when using the density from the literature ($\sim$3.1–3.44 g cm^{-3}) or even the value given by the manufacturer ($\sim$3.1 g cm^{-3}), the calculated energy losses show significant discrepancy from the measured data. Therefore the calculated average density value (2.71 $\pm$ 0.11 g cm^{-3}) using RBS technique is supported to use as a standard value in the applications (e.g. calculation of energy loss and number of target nuclei). This value is also very similar to the one in ref [12], although the preparation method of the studied films was different.

PIXE analysis

Particle induced X-ray emission measurements were carried out to examine impurities and other trace elements what the sample might have contained. The preparation method of these thin foils is based on the reaction between dichlorosilane and NH$_3$ so some Cl content can be remained in the samples during the process. Figure 3 shows the PIXE spectra of the 200 and 500 nm thick Si$_3$N$_4$ foils.

Table 2 shows the chlorine concentrations obtained from the PIXE measurements. The measured Si$_3$N$_4$ foils contained chlorine impurities which might originate from the dichlorosilane starting material (or occurred during the post-production treatments).
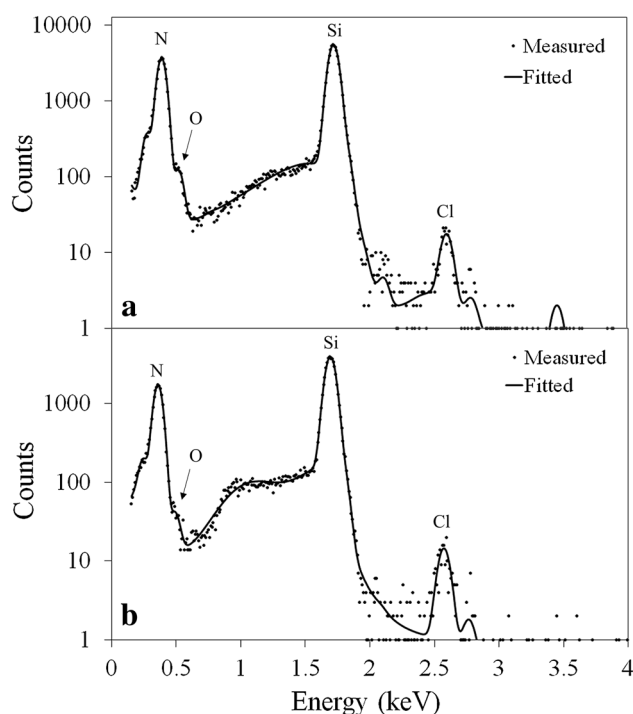

Fig. 3 The PIXE spectra of **a** 200 nm and **b** 500 nm thick Si$_3$N$_4$ foils. The measured data was fitted with the GUPIXWIN code

Table 2 The measured chlorine concentration of the different Si_3N_4 films

Sample	Chlorine concentration (ppm)
Norcada 100 nm	3810 ± 495
Norcada 200 nm	2910 ± 350
Silson 200 nm	4085 ± 435
Silson 500 nm	2940 ± 620

Uncertainty of weighted average of concentration values were calculated based on the error of fitting process and the standard deviation of data

The PIXE measurements showed that there was oxygen impurity in the samples in the range of ~ 2000–3000 ppm, in all cases. Contrary to the case of the 500 nm thick foils where the oxygen was in a silicon-oxide layer, the source of this oxygen is not known; it can be in the material or on the surface as an environmental contamination as well.

Conclusions

In this study, the determination of the density of some commonly used thin Si_3N_4 films have been reported using ion-beam analytical methods, such as RBS, PIXE spectroscopy and STIM.

By RBS and profilometry measurements we determined the density and stoichiometry of the different LPCVD deposited Si_3N_4 foils. We found that the density of the thin Si_3N_4 significantly differ from the density of the bulk material, generally it is about 15–20 % lower. STIM measurements were performed in order to verify the density of the foils. We found that the calculated He^+ energy losses on the different Si_3N_4 thin films match very well with the experimental results when calculation use the densities determined by the RBS method. The PIXE measurements showed chlorine impurities (~ 0.3–0.4 %) which is probably originated from the starting material, during the production.

In conclusion, the combination of IBA techniques and profilometry can provide valuable information on the density of the films produced by various processing methods. We suggest the value of 2.71 ± 0.11 g cm^{-3} as a density of Si_3N_4 films in different applications (e.g. calculation of energy loss and number of target nuclei).

References

1. Milek JT (1971) Silicon nitride for microelectronic applications. IFI/Plenum, New York
2. Bouwstra S, Legtenberg R, Tilmans HAC, Elwenspoek M (1990) Resonating microbridge mass flow sensor. Sens Actuators A 21–23:332–335
3. Sekimoto M, Yoshihara H, Ohkubo T (1982) Silicon nitride single-layer X-ray mask. J Vac Sci Technol 21:1017–1021
4. van Bebber H, Borucki L, Farzin K, Kiss ÁZ, Shulte WH (1998) Total cross section of the 14 N(d, pγ)15 N nuclear reaction for analytical applications. Nucl Instrum Methods B 136–138:72–76
5. Pellegrino S, Beck S, Trousland Ph (2004) Differential cross-sections for nuclear reactions 14 N(d, p5)15 N, 14 N(d, p0)15 N, 14 N(d, α0)12C and 14 N(d, α1)12C. Nucl Instrum Methods B 219–220:140–144
6. Csedreki L, Uzonyi I, Szikszai Z, Gyürky G, Szíki GÁ, Kiss ÁZ (2014) Nucl Instrum Methods B 328:20–26
7. Taft EA (1971) Characterization of silicon nitride films. J Electrochem Soc 118:1341–1346
8. Rosler RS (1977) Low pressure CVD production processes for poly nitride and oxide. Solid State Technol 20:63
9. Li W-T, McKenzie DR, McFall WD, Zhang Q-C (2001) Effect of sputtering-gas pressure on properties of silicon nitride films produced by helicon plasma sputtering. Thin Solid Films 384:46–52
10. Verlaan V, Verkerk AD, Arnoldbik WM, van der Werf CHM, Bakker R, Houweling ZS, Romijn IG, Borsa DM, Weeber AW, Luxembourg SL, Zeman M, Dekkers HFW, Schropp REI (2009) The effect of composition on the bond structure and refractive index of silicon nitride deposited by HWCVD and PECVD. Thin Solid Films 517:3499–3502
11. Petalas J, Logothetidis S, Markwitz A, Paloura EC, Johnsonc RL, Fuchsd D (1993) Characterization of SiN thin films with spectroscopic ellipsometry. Phys B 185:342–347
12. Markwitz A, Baumann H, Krimmel EF, Bethge K, Misaelides P (1993) Characterisation of thin sputtered silicon nitride films by NRA, ERDA, RBS and SEM. Fresenius J Anal Chem 346:177–180
13. Temple-Boyer P, Rossi C, Saint-Etienne E, Scheid E (1998) Residual stress in low pressure chemical vapor deposition SiN$_x$ films deposited from silane and ammonia. J Vac Sci Technol A 16:4
14. Oxford Microbeams Ltd (1996) http://www.microbeams.co.uk/
15. Rajta I, Borbély-Kiss I, Gy Mórik, Bartha L, Koltay E, Kiss ÁZ (1996) The new ATOMKI scanning proton microprobe. Nucl Instrum Methods B 109(110):148–153
16. Simon A, Huszank R, Novák M, Pintye Z (2010) Investigation of hydrogen depletion of organic materials upon ion beam irradiation by simultaneous micro-RBS and micro-ERDA techniques. Nucl Instrum Methods B 268:2197–2201
17. Simon A, Sulyok A, Novák M, Juhász G, Lohner T, Fried M, Barna A, Huszank R, Menyhárd M (2009) Investigation of an ion-milled Si/Cr multilayer using micro-RBS, ellipsometry and AES depth profiling techniques. Nucl Instrum Methods B 267:2212–2215
18. Uzonyi I, Rajta I, Bartha L, Kiss ÁZ, Nagy A (2001) Realization of the simultaneous micro-PIXE analysis of heavy and light elements at a nuclear microprobe. Nucl Instrum Methods B 181:193–198
19. Zs Kertész, Szikszai Z, Uzonyi I, Simon A, Kiss ÁZ (2005) Development of a bio-PIXE setup at the Debrecen scanning proton microprobe. Nucl Instrum Methods B 231:106–111
20. The 5 MV Van de Graaff generator of Atomki technical report (1979), MTA Atommag Kutató Intézete, Debrecen

21. Mayer M (1997) SIMNRA user's guide, Tech. Rep. IPP 9/113, Max–Planck–Institut für Plasmaphysik, Garching
22. Maxwell JA, Teesdale WJ, Campbell JL (1995) The Guelph PIXE software package II. Nucl Instrum Methods B 95:407–421
23. Ziegler JF, Ziegler MD, Biersack JP (2010) SRIM—The stopping and range of ions in matter. Nucl Instrum Methods B 268:1818–1823
24. Dytlewski N, Cohen DD, Evans PJ, Prince KE, Collins GA, Barbe C, Cassidy DJ (2000) A comparative study of different IBA techniques for determining the thickness of thin SiO_2 films. Nucl Instrum Methods B 161–163:573–577