Determination of nitrogen content within silicon nitride thin films synthesised by hot-wire chemical vapour deposition

Clive J. Oliphant\textsuperscript{1,2}, Theo Muller\textsuperscript{2}, Abdulghaaliq Adams\textsuperscript{2}, Mandla Msimanga\textsuperscript{3} and Christopher J. Arendse\textsuperscript{2}

\textsuperscript{1}National Metrology Institute of South Africa
Private Bag X34, Lynnwood Ridge, Pretoria, 0040, South Africa
Phone: 012 841 2607 Fax: 012 841 2131
e-mail: coliphant@nmisa.org

\textsuperscript{2}Department of Physics, University of the Western Cape, Private Bag X17, Bellville, 7535

\textsuperscript{3}iThemba labs (Guateng), Private Bag X11, WITS 2050

Abstract

Hydrogenated silicon nitride thin films (SiN\textsubscript{x}) have enjoyed considerable industrial applications such as insulators, dielectric material, barrier coatings and as antireflective and passivation coatings on solar cells. The wide application scope of SiN\textsubscript{x} is due to their wide range of optoelectronic properties and structural properties. One of the most important parameters determining the eventual properties of SiN\textsubscript{x} thin films is the nitrogen to silicon ratio (x = N/Si) within the film. Analytical techniques typically used to measure the N/Si value include Fourier transform infrared spectroscopy, elastic recoil detection (ERD), secondary ion mass spectroscopy and x-ray photoelectron spectroscopy. However, energy dispersive x-ray spectroscopy (EDS) is experiencing rapid development in its capability to analyse low atomic number elements. In this study we report on the capability of EDS within a scanning electron microscope to analyse the N/Si ratio of SiN\textsubscript{x} thin films deposited on Corning glass substrates by the hot-wire chemical vapour deposition technique. We compared the EDS results with the more established heavy ion ERD analysis performed at iThemba Labs. The results within this study show that EDS can be used to determine the N/Si ratio of the SiN\textsubscript{x} thin films. However, there are still challenges with EDS analysis such as the substrate effects which become more prominent for SiN\textsubscript{x} films with thickness below 300 nm. Nevertheless, with the increasing availability and development of scanning electron microscopes and the enhancing sensitivity of x-ray detectors at lower acceleration voltages, EDS may become more relevant for the rapid quantification of low atomic number elements of samples with sizes less than 300 nm.

Keywords: silicon nitride, thin films, elastic recoil detection, energy dispersive x-ray spectroscopy
1. Introduction

Amorphous silicon nitride (SiNx), where x is the N/Si ratio, is an important dielectric which has enjoyed active research interest during the last few decades. SiNx has been applied industrially as surface and bulk passivation layers [1], thin film transistors [2] and antireflection coatings [3] and has shown promise as a light emitting material [4]. The wide application scope of SiNx can be attributed to its molecular composition, structural properties and optoelectronic properties, all of which can be tuned by varying the thin film synthesis conditions. Plasma enhanced chemical vapour deposition (PECVD) is the industrial workhorse used to fabricate SiNx thin films [1]. However, an alternative technique known as hot-wire chemical vapour deposition (HWCVD) offers superior growth rates [3], which favour reduced production costs.

Generally, the nitrogen to silicon ratio x is one of the most important factors governing the SiNx optoelectronic properties. In general, the N/Si ratio is determined from Rutherford backscatter spectroscopy (RBS), heavy ion elastic recoil detection (ERD) [5], FTIR [6] or indirectly from the film refractive index [7]. However, the proportionality constants necessary for quantification from FTIR varies with film composition [8], and the refractive index is influenced by the film density which, in turn, may also depend on the deposition technique [9]. Currently, scanning electron microscopes (SEM) are becoming increasingly accessible and, coupled to a SEM in most cases is an energy dispersive x-ray spectroscopy (EDS) detector. EDS is used to identify and quantify elemental compositions of various elements with an atomic number larger than 4 (Be).

Despite its immense development for determining elemental compositions of bulk materials, EDS on thin films during SEM characterization less attention. This can be attributed to the beam penetration depth, issues relating to the homogeneity of the thin film (which will influence the quantification) and relatively high inaccuracies for low atomic number elements such as C. Nevertheless, with the advent of more sensitive detectors and enhanced detection levels at low acceleration voltages, EDS may be used as an alternative option to determine the elemental composition of SiNx thin films. In this contribution we will explore the capabilities of energy dispersive x-ray spectroscopy (EDS) in determining the N content of SiNx thin films. A comparison will be drawn between the EDS findings and the more established time-of-flight elastic recoil detection analysis (ToF-ERDA).

2. Experimental procedure

2.1 Deposition conditions

SiNx thin films were deposited simultaneously on Corning 7059 and Si (100) substrates using a high vacuum MVSystems HWCVD system described elsewhere [10]. Figure 1 shows a schematic of the HWCVD system and examples of SiNx samples with varying Si and N contents and thicknesses. Two deposition regimes were followed in this study: in the first series the NH3 flow rate was varied and in the second series the hydrogen (H2) flow rate was varied. The filament temperature amounted to ~ 1470 °C as measured by a two-colour pyrometer. The deposition pressure and substrate temperature were fixed to 100 µbar and 240 °C, respectively.
2.2 Thin film characterization

The elemental composition of the SiN$_x$ thin films were determined using an OXFORD INCA energy dispersive x-ray spectroscopy (EDS) system attached to a Zeiss Leo 1525 field emission gun scanning electron microscope (FEG-SEM) housed at the NMISA. EDS analysis is based on the measurement of X-rays emitted from the atoms composing the sample under irradiation from a high energy (usually 10-20 keV) electron beam. Specifically, electrons from the incident electron beam knocks out electrons orbiting the nucleus within the atom of the sample. The atom consequently becomes unstable and in order to reach its ground energy state, electrons from a higher energy shell replaces the ejected electron, resulting in the emission of an x-ray photon with energy equal to the difference of the two participating energy shells, which is unique for a given atom. The emitted x-rays are then detected and converted to a voltage pulse proportional to the x-ray photon energy by a cooled lithium-drifted silicon Si (Li) solid state detector.

Determining the energy and counts of the characteristic x-rays therefore provides a means of identifying and quantifying the atoms present. However, elemental quantification in the case of EDS is achieved by choosing the suitable counting time for x-ray accumulation and optimum microscope conditions. Generally, the minimum acceleration voltage should be more than twice the highest excitation energy needed for x-ray generation. The beam current should be in the order of a few nA and the working distance where maximum x-ray count rates are achieved are also important operating parameters.

Approximating the unknown composition requires correction for the matrix within which the element to be analysed resides. For a more in-depth discussion the reader is referred to Goldstein et al. [11]. Briefly, these matrix effects can be divided into atomic number (Z), x-ray absorption (A) and x-ray fluorescence (F) effects. Modern EDS systems come pre-loaded with a database of theoretically calculated and experimental standard measurements which were performed by the manufacturer on an instrument with the software.
In most practical cases, so-called semi-quantitative or “standardless” elemental analysis using EDS is obtained by determining the composition of the sample relative to a preloaded standard. A further complication with EDS analysis is the beam penetration depth, which is especially important for the elemental quantification of thin films. Monte Carlo simulations [12] were performed in order to determine the expected electron beam penetration depth within a SiN$_x$ thin film. The modelling conditions were: a spot size of 10 nm, accelerating voltage of 6 kV and a number of 1000 electrons. Figure 2 shows the Monte Carlo results for expected Si-rich and N-rich samples. The X-rays used by EDS for quantification originate from the total blue area. We therefore expect that the Si from the substrate will not interfere with the analysis for SiN$_x$ thin films with thicknesses greater than 300 nm. EDS was performed on SiN$_x$ deposited on glass to validate that the substrate does not interfere with the analysis. Figure 3 compares EDS spectra of the Corning substrate and typical SiN$_x$ samples. No detectable B, Al and Ba are present in the EDS spectra of SiN$_x$ samples, indicating that the substrate elemental contributions are excluded from the analysis. The O and C signals in the SiN$_x$ EDS spectra originate from the surface contamination of the SiN$_x$ thin films as shown by x-ray photoelectron spectroscopy (results to be published elsewhere).

![Figure 2: Monte Carlo simulations of the expected SEM beam penetration depth and profile for (a) Si-rich and (b) N-rich SiN$_x$.](image)
Figure 3: EDS spectra of (a) Corning substrate and (b) Si$_x$N$_x$ films deposited at different NH3 flow rates (vertically offset for clarity).

Based on the Monte Carlo simulations and the EDS analysis shown in Figure 3, the microscope conditions for EDS were fixed at 6 kV, an aperture size of 30 µm and a working distance of 10 mm. A pure Si standard was used as the quantification optimization element to monitor the electron beam stability. At these EDS beam conditions, analysis of an AlN reference material (with a composition of 33 wt. % N) yielded a nitrogen composition of 31.32 wt. % within standard deviation of 1.58 wt. %. All the Si$_x$N$_x$ films investigated in this study have thicknesses > 350 nm.

Time-of-flight elastic recoil detection analysis (ToF-ERDA) was also performed using $^{73}$Cu$^{7+}$ ions at 26.3 MeV with a 10 nA current in order to verify the N and Si content. The projectiles were produced in a 6 MV tandem accelerator at iThemba labs, Gauteng. During ToF-ERDA energy of recoils from the measured ToF are calculated. Calibration then entails ToF calibration and then conversion of the ToF spectra into energy spectra. For ToF calibration the time-of-flight of at least three different recoil ions from pure Si, C-graphite and Au/Si samples needs to be determined. By means of kinematic considerations [13], calculations are performed on the SIMNRA software package to determine the ToF of those recoils knocked off the surface region of a sample, referred to as the high energy edge recoils. Since the mass of the ions are known, the velocity can be determined. Given that the flight distance is fixed at 0.6 m, the ToF (in ns) can then be calculated. Then, from a plot of the ToF (ns) vs. ToF (channels) the calibration parameters (slope and intercept) can be obtained, which are used to convert the ToF spectra in channels to ToF spectra in ns. Finally, the ToF spectra are converted into energy spectra for any ion using:

$$E = \frac{1}{2}m(L/ToF)^2$$

where $L$ is the ToF distance fixed at 0.6 m and $m$ is the mass of the ion.
3. Results and discussion

Figure 4 presents ToF-ERD elemental depth profiles of SiNₓ thin films. Similar to the EDS analysis, oxygen and carbon were present in the SiNₓ thin films. However, ERD reveal that C and O are surface impurities while the film bulk is composed of Si and N. This finding is promising considering that SiNₓ is expected to be an effective water and oxygen barrier for plastic electronics [14]. Interestingly, a high concentration of N is present at the SiNₓ/c-Si interface. We performed cross-sectional electron energy loss spectroscopy in a high resolution transmission electron microscope (results to be published in Applied Surface Science) and found that there exists a N-rich layer sandwiched by the SiNₓ film and c-Si substrate. The presence of a N-rich interface is attributed to the in-diffusion of N into the oxidized c-Si substrate. Fukuda et al. [15] also reported similar findings in their oxynitridation of a Si (100) wafer.

![ToF-ERDA elemental profiles of representative SiNₓ films](image)

Figure 5 presents the comparison between ERD and EDS in determining the N content within SiNₓ films deposited at different NH₃ and H₂ flow rates. The sample inhomogeneity at different areas of the thin film is reflected in the large standard deviation. Nevertheless, the two techniques are complimentary in determining the N content of SiNₓ thin films. According to the data shown in Figure 5, the SiNₓ films become more N-rich with an increasing NH₃ flow, indicating that the NH₃ gas dissociation is efficient during HWCVD. Mahan et al. [6] also reported a similar observation in their HWCVD of SiNₓ studies. The efficient dissociation of gas molecules during HWCVD is attributed to the effective catalytic decomposition process at the heated filament and to secondary reactions en route to the substrate. However, figure 5b reveals that by increasing the H₂ flow rate at constant NH₃ and SiH₄ flow rates results in SiNₓ films with a superior N-concentration. The addition of H₂ to the chamber leads to a higher atomic hydrogen concentration, which has an etching effect on the filament, consequently freeing up silicide contaminated active sites to allow for more efficient dissociation of NH₃ [16] and consequently more N becoming available for the synthesis.
4. Conclusion

The N-content of SiNₓ thin films deposited by HWCVD was determined using EDS and compared to ToF-ERD. Despite the SiNₓ thin film inhomogeneity, good agreement between the two independent techniques was obtained. EDS within the SEM is a promising method for determining the N-content of SiNₓ thin films provided that the films are thicker than the expected electron beam penetration path at the microscope operating conditions.

5. References


