Journal of the European Ceramic Society **15** (1995) 313–318

0955-2219/95/$9.50

Determination of Oxide Thickness on an Si_2N_2O–ZrO_2 Composite by Spectroscopic Ellipsometry

M. Heim,[a] H. Arwin,[b] J. Chen[a] & R. Pompe[c]

[a] Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

[b] Laboratory of Applied Physics, Department of Physics and Measurement Technology, Linköping Institute of Technology, S-581 83 Linköping, Sweden

[c] Swedish Ceramic Institute, Box 5403, S-402 29 Göteborg, Sweden

(Received 13 May 1994; accepted 20 June 1994)

Abstract

Initial oxidation behaviour of an Si_2N_2O–ZrO_2 composite material has been investigated by spectroscopic ellipsometry (SE), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The material was exposed to air in the temperature range of 1000–1450°C and the oxide layer thickness was determined by SE using the Bruggeman effective medium approximation for the modelling of the oxide layer. It was shown that the oxide film on a porous Si_2N_2O–ZrO_2 material can be characterized by SE. The results provide important information about film growth in the initial stage of oxidation of this composite. The optical constants for the composite and ZrO_2 were determined.

1 Introduction

Silicon oxynitride ceramics have good oxidation, corrosion, and thermal shock resistance which makes them interesting for high temperature applications.[1] A low-cost Si_2N_2O–ZrO_2 composite, fabricated by the nitrided pressureless sintering technique (NPS) at the Swedish Ceramic Institute with $ZrSiO_4$ and Si as starting materials, according to eqn (1) was investigated.[2,3]

$$ZrSiO_4 + 3\,Si + 2\,N_2 \rightarrow 2\,Si_2N_2O + t\text{-} + m\text{-}ZrO_2 \quad (1)$$

(t tetragonal, m monoclinic)

Initial oxidation kinetics of nitride materials is expected to be important for the understanding of the entire oxidation mechanism of the material. The measurement of the oxide growth, however, is usually difficult because the oxidized layer is too thin to be detected by gravimetric methods.

To follow the initial stage of oxidation, spectroscopic ellipsometry (SE) has been anticipated to be useful for studying the growth of the oxide layer on this ceramic material. This non-contact and non-destructive optical method, has been increasingly used to study thin film materials. Several investigations on ceramic film deposited on single crystal Si wafers have been done.[4–8] However, to our knowledge, no SE measurement aiming at evaluation of the oxidation process on ceramic composite systems, such as the Si_2N_2O–ZrO_2 material, has been reported.

The advantage in use of spectroscopic ellipsometry in comparison to single wavelength ellipsometry is that by achieving a good fit of the model the probability of receiving 'true' values increases enormously.

The objective of this work has been to demonstrate that SE is a potential method to evaluate the initial oxidation kinetics, not only for monolithic ceramic materials, but also for porous ceramic composites. The kinetic data is useful for the evaluation of internal and external oxidation of the porous composite.

2 Experimental

2.1 Sample preparation

The bulk density of the as-received material was determined to be 2·55 g/cm^3 or 72·4% of the theoretical density and the open porosity of the material is 24·5%.

For the ellipsometry measurement the Si_2N_2O–ZrO_2 composite (3 × 5 × 1 mm) and ZrO_2-ceramic specimen (10 × 10 × 3 mm) were cleaned with a standardized procedure. The samples were

ground and carefully polished with diamond spray down to 0·25 μm fineness and cleaned in water, trichlorethene and acetone in an ultrasonic bath. Afterwards, the samples were cleaned in a solution of H_2O:H_2O_2:NH_3 (25%) = 5:1:1 and a solution of H_2O:H_2O_2:HCl (conc) = 6:1:1, respectively, at 80°C for 5 min and finally washed with distilled water. The samples were dried in dry nitrogen and then oxidized in an alumina tube furnace in static air at 1000, 1250 and 1450°C, respectively, and taken out periodically for the SE measurements.

2.2 Microstructural analysis

The chemical composition of the as-received and in the thermobalance oxidized material was characterized by using X-ray diffractometry (XRD, SIEMENS D5000). The micro-morphology was investigated by scanning electron microscopy (SEM, JEOL JSM-5300).

2.3 Ellipsometry

Only a brief description on SE is given here and a detailed background to ellipsometry can be found elsewhere.[9,10] The technique is based on the polarization changes that occur upon oblique reflection of polarized light. The quantity an ellipsometer measures is the so called complex reflectance ratio $\rho = \tan\psi e^{i\Delta} = R_p/R_s$, where ψ and Δ are the ellipsometric angles, and R_p and R_s are the complex reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively. ψ and Δ can readily be determined with a precision better than 0·01° and once ρ has been measured it can be analyzed with respect to the parameters examined. The most common parameters which are quantified by ellipsometry are film thickness and optical constants of thin films or film-free bulk materials.

In this study we have used a rotating analyser spectroscopic ellipsometer (J. A. Woollam Co.) for measuring ψ and Δ in the wavelength range 3000–8000 Å at an angle of incidence of 68°. Figure 1 shows the principle arrangement of the instrument.

Table 1. Surface phase composition at different oxidation temperatures for an Si_2N_2O–ZrO_2 material

Temperature (°C)	*Phase composition*				
	Si_2N_2O	m-ZrO_2	t-ZrO_2	$ZrSiO_4$	SiO_2
as received	s	s	m	-	-
1000	s	s	m	-	w
1300	w	w	w	m	w
1450	w	w	m	m	w
1600	w	w	w	vs	w

w-weak, m-medium, s-strong, vs-very strong

3 Results and Discussion

3.1 Elemental composition

After exposing selected samples in the thermobalance, the phase compositions were investigated by XRD. The penetration depth was calculated to be 56 μm at $2\Theta = 65°$ (which is much higher than the medium grain size), with the assumption that the material is completely converted to $ZrSiO_4$ and SiO_2. Table 1 shows the results for the exposure for 7 h at the respective temperatures.

The results obtained from XRD investigations show that the chemical reaction of the Si_2N_2O–ZrO_2 system during oxidation can be divided into two temperature areas.

(1) ≈ 1000°C

$$Si_2N_2O\text{–}ZrO_2 + 3/2\,O_2 \rightarrow 2\,SiO_2 + ZrO_2 + N_2 \quad (2)$$

At 1000°C the temperature is too low for ZrO_2 to take part in the reaction. This means that only Si_2N_2O contributes to the reaction and cristobalite (SiO_2) is formed. From other work done on this material.[11,12] it is known that at this temperature external and internal oxidation of the material takes place due to the open porosity.

(2) ≥ 1250°C

$$Si_2N_2O\text{–}ZrO_2 + 5/2\,O_2 \rightarrow ZrSiO_4 + SiO_2 + ZrO_2 + N_2 \quad (3)$$

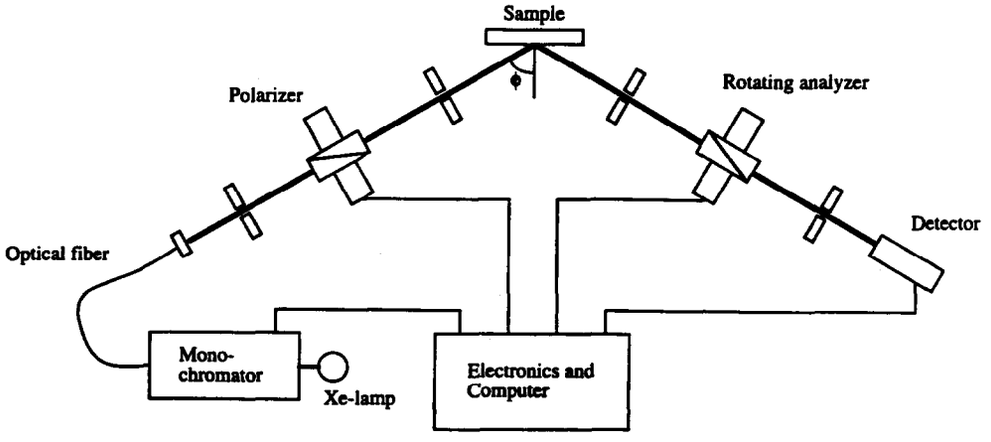

Fig. 1. Spectroscopic ellipsometer of the rotating analyzer type.

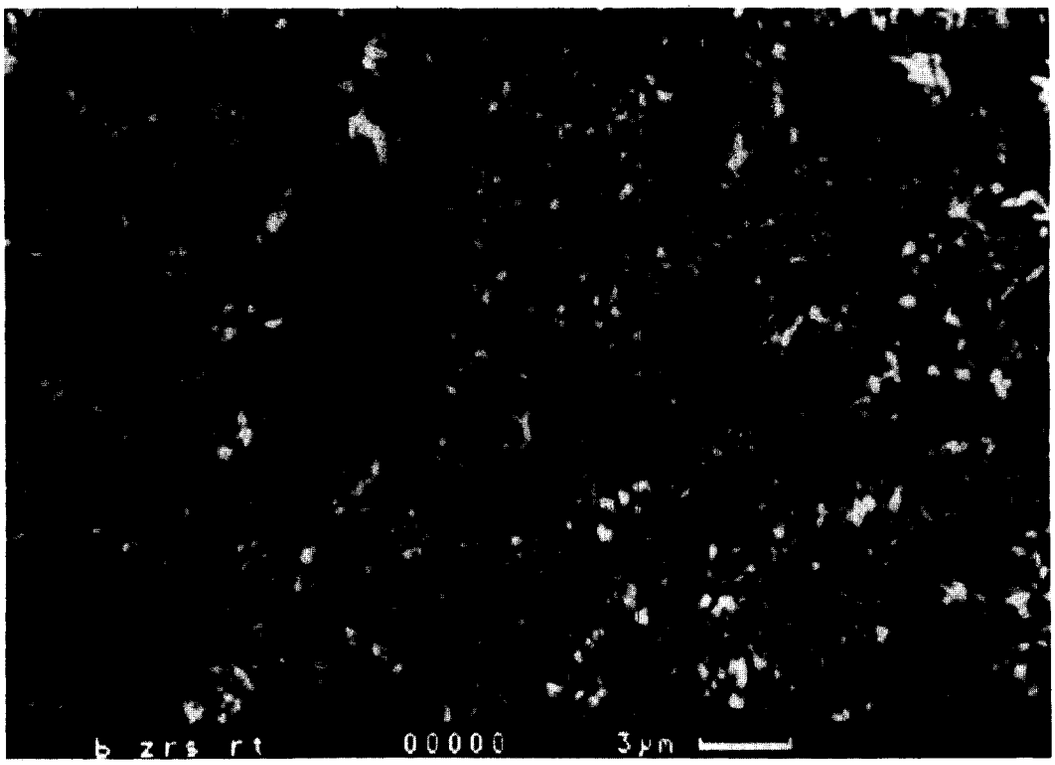

Fig. 2. Backscattered SEM image of a polished surface of an as-received Si_2N_2O–ZrO_2 material (light spots ZrO_2, dark areas Si_2N_2O and pores).

At temperatures ≥ 1250°C zircon ($ZrSiO_4$) and cristobalite are formed as the main reaction products. After initial weight gain the weight stabilizes which is thought to be caused by the formation of a dense oxide film containing $ZrSiO_4$, preventing further oxidation. The higher the temperature the less weight gain occurred.

3.2 Microstructural analysis

Figure 2 shows an SEM image of the surface of the as-received material. The porosity of the material can be clearly seen. Figure 3 shows schematic model of the as-received material, also in cross section.

3.3 Ellipsometric measurement and optical modelling

From the SEM image shown in Fig. 2 it can be seen that the surface is quite porous compared to monolithic ceramics like Si or Si_3N_4.[13] This is caused by the presence of open porosity. Because the grain size (0·5–2 µm) is larger than the selected range of wavelength of incident light, it was assumed that the surface is locally flat and the radius of curvature in a general point of the rough surface is much greater than the selected range of wavelength. The effects of surface roughness can then be neglected in the calculations.

Figure 4 shows the models of samples exposed to 1000°C, and ≤ 1250°C, respectively, which are assumed in the calculations.

At 1000°C only the thickness of the formed SiO_2 is measured. Because ZrO_2 does not react at this temperature, the index of refraction does not change and does not contribute to a change of polarization.

At all temperatures, ZrO_2 could be detected in the surface layer. Because no data for the index of refraction is available for $ZrSiO_4$ in the wavelength range needed for the modelling, the top

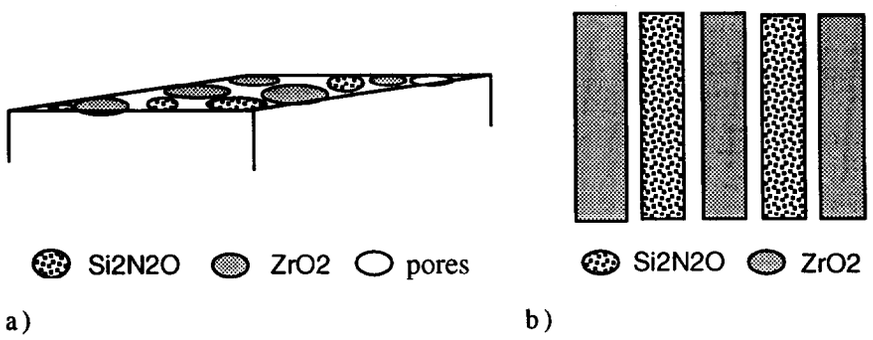

Fig. 3. Schematic illustration of the composition of as-received Si_2N_2O–ZrO_2 material. (a) Top view, (b) cross section.

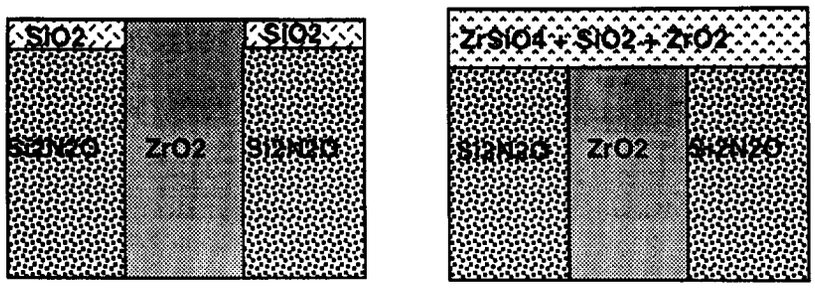

Fig. 4. Models used for oxidation of a Si_2N_2O–ZrO_2 material at (a) 1000°C and (b) ≥ 1250°C.

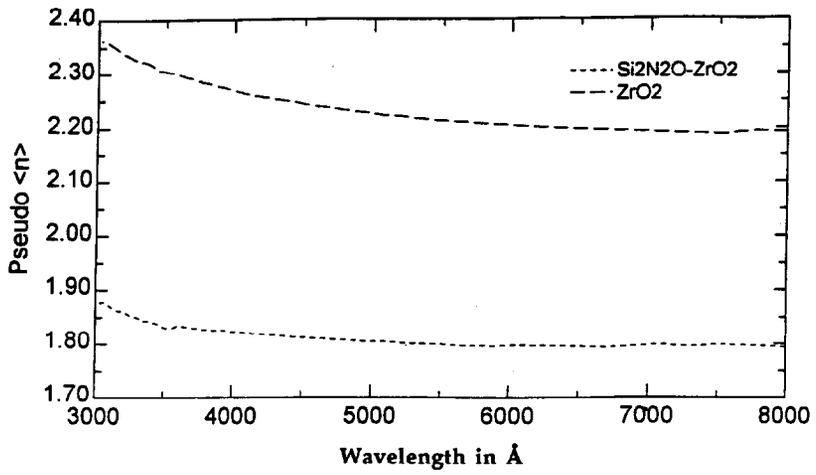

Fig. 5. Refractive indices as function of wavelength for ZrO_2 and Si_2N_2O–ZrO_2 at room temperature.

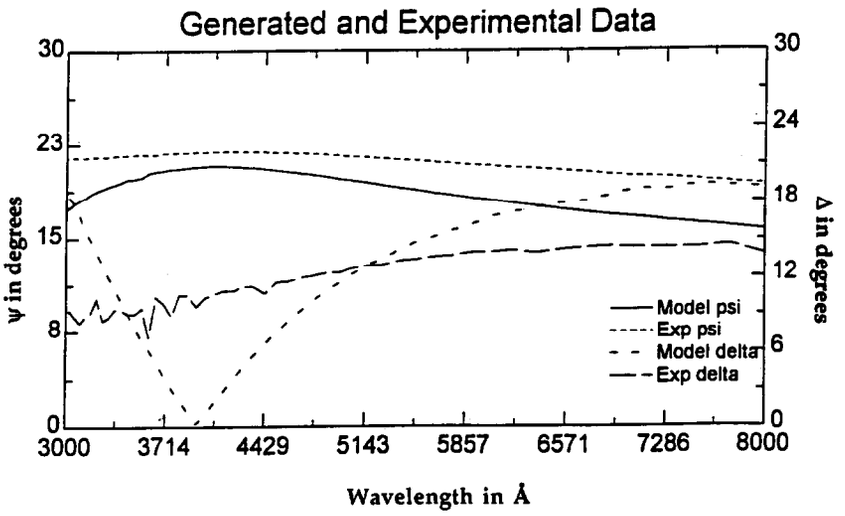

Fig. 6. An example of optical modelling for a sample of Si_2N_2O–ZrO_2 oxidized for 60 min at 1250°C.

layer was modelled on the assumption that it was a physical mixture consisting of two distinct phases, SiO_2 and ZrO_2, and modelled with the Bruggeman effective medium approximation (EMA).[14] Accordingly, the effective (macroscopic) refractive index n of $ZrSiO_4$ can be obtained from the following equations:

$$f_{SiO_2}\frac{n_{SiO_2}^2 - n^2}{n_{SiO_2}^2 + 2n} + f_{ZrO_2}\frac{n_{ZrO_2}^2 - n^2}{n_{ZrO_2}^2 + 2n} \quad (4)$$

and

$$f_{SiO_2} + f_{ZrO_2} = 1 \quad (5)$$

where f_{SiO_2} and f_{ZrO_2} are the relative volume fractions of SiO_2 and ZrO_2 in the material. The refractive index for SiO_2 is taken from the literature,[15] while the refractive index for ZrO_2 was determined experimentally.

Samples of pure ZrO_2 and unexposed Si_2N_2O–ZrO_2 were measured with SE and their

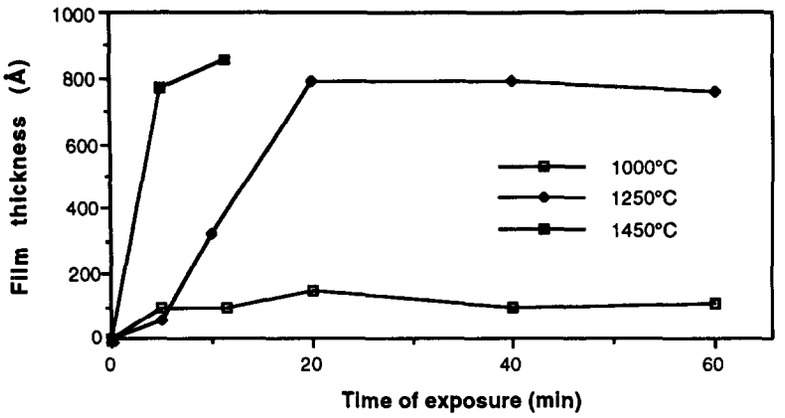

Fig. 7. Oxide film thickness as function of temperature and time of exposure for the Si_2N_2O–ZrO_2 material.

refractive indices were determined by a numeric inversion of $\rho = \tan \psi e^{i\Delta}$ in the wavelength range from 3000 to 8000 Å with results as shown in Fig. 5. Oxide thickness and film composition of Si_2N_2O–ZrO_2 samples were determined with least square regression procedures in a three-phase (Ambient-layer-substrate) model.

After oxidation of the Si_2N_2O–ZrO_2 samples, the thicknesses of the formed $ZrSiO_4/SiO_2$ surface layer were determined ellipsometrically. Figure 6 shows an example of the data fitting using the three-phase model described above. The ψ values of the model fit the experimental data closely and the Δ values show a reasonably good fit, considering the small scale given in the figure. Therefore the error of the determined thickness would be marginal, as described elsewhere.[16]

Figure 7 shows the results obtained for the external oxide scale thicknesses at different temperatures. After exposing the samples for more than 11 min at 1450°C, it was impossible to align the sample due to severe scattering of the incoming light and no results could be obtained.

The measured values of the external oxide film thickness after short exposure time are consistent with the weight gain measurements and SEM investigation.[11] At 1000°C a continuous oxidation of the pore walls occurs at a relatively low constant rate — thus the initial film thickness at the outer specimen surface does not change significantly within the time frame of 1 h. At higher temperatures (≥ 1250°C) the starting oxidation rate is much higher and thus, the thickness of the initial oxide film reaches rapidly a higher level at the outer surface. After that oxygen will diffuse into the interior and oxidize the internal pore surface. SEM observations indicate that a thicker oxide scale has been formed in the surface region of the sample.

Investigations are under way to find a quantitative correlation between the oxide film thickness values obtained through VASE and those directly observed with other methods.

4 Conclusions

(1) The refractive indices of ZrO_2 and Si_2N_2O–ZrO_2 have been determined.
(2) The film thickness of $ZrSiO_4$ formed on oxidized samples has been measured.
(3) A determination of the film thickness is possible on this rather porous ceramic material.

Acknowledgements

Thanks to Dr C. O'Meara (Department of Physics, Chalmers University of Technology) for the SEM investigations. Financial support from the Swedish National Board for Industrial and Technical Development is gratefully acknowledged (Contract No. 88-04709P)

References

1. Hoggard, D. B., Park, H. K., Morrison, R. & Slasor, S., O–Zirconia and its refractory application. *Am. Ceram. Soc. Bull.*, **69** [7] (1990) 1163–6.
2. Pompe, R., Method for producing ceramic composite materials containing silicon oxynitride and zirconium oxide. U.S. Pat. 438 416, 1 June 1987.
3. Pompe, R. & Carlsson, R., *Reaction Sintered Si_2N_2O/ZrO_2 Composite*. Abstract 90th AcerS Meeting, 83-C-88, 1988.
4. Knolle, W. R., Correlation of refractive index and silicon content of silicon oxynitride films. *Thin Solid Films*, **168** (1989) 123–32.
5. Snyder, P. G., Xiong,Y. -M., Woollam, Y. A., Al-Jumaily, G. A. & Gagliardi, F. J., Graded refractive index silicon oxynitride thin film characterized by spectroscopic ellipsometry. *J. Vac. Sci. Technol. A*, **10** (4) (1992) 1462-6.
6. Xiong, Y. -M., Snyder, P. G., Woollam, J. A., Al-Jumaily, G. A., Gagliardi, F. J. & Mizerka, L. J., Controlled index of refraction silicon oxynitride films characterized by variable angle spectroscopic ellipsometry. *Thin Solid Films*, **206** (1991) 248–53.
7. Xiong, Y. -M., Snyder, P. G., Woollam, J. A., Al-Jumaily, G. A., Gagliardi, F. J. & Mizerka, L. J., Optical characterization of silicon oxynitride thin films by variable angle spectroscopic ellipsometry. *Surface and Interface Analysis*, **18** (1992) 124–8.

8. Xiong, Y.-M., Snyder, P. G., Woollam, J. A., & Krosche, E. R., Silicon nitride/silicon oxynitride/ silicon dioxide thin film multilayer characterized by variable angle spectroscopic ellipsometry. *J. Vac. Sci Technol. A*, **10** (4) (1992) 950–4.
9. Azzam, R. M. A. & Bashara, N. M., *Ellipsometry and Polarized Light*, North-Holland, Amsterdam, 1977.
10. Azzam, R. M. A., *Selected Papers on Ellipsometry*, SPIE Optical Engineering Press, Bellingham, 1991.
11. Heim, M., Pompe, R., Arwin, H. & Chen, J., High temperature oxidation behaviour of an Si_2N_2O–ZrO_2 composite, In *Proc. of the 5th International Symposium on Ceramic Materials & Components for Engines*, Shanghai, 1994.
12. O'Meara, C., Heim, M. & Pompe, R., The oxidation behaviour of a porous Si_2N_2O–ZrO_2 composite material, submitted for publication.
13. Chen, J., Arwin, H., Heim, M. & Sjöberg, J., Oxidation of pure Si_3N_4: spectroscopic ellipsometry and glancing angle X-ray diffraction studies. In *Proc. of the International Conference on Silicon Nitride-Based Ceramics*, Stuttgart, 4–6 October, 1993, Trans Tech Publications, 1994, pp. 301–6.
14. Kuiper, E. T., Koo, S. W., & Habraken, F. H. P. M., Correlation of refractive index and silicon content of silicon oxynitride films. *J. Vac. Sci.*, **B1**, (1983) 62.
15. Maltison, I. H., Interspecimen comparison of the refractive index of fused silica. *J. Opt. Soc. Am.*, **55** (1965) 1205–9.
16. Chen, J., Arwin, H. & Lindqvist, O., Spectroscopic ellipsometry measurement of the oxide thickness on silicon nitride ceramics. In *Proc. of the 5th International Symposium on Ceramic Materials & Components for Engines*, Shanghai, 1994.