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# Comparison of techniques to characterise the density, porosity and elastic modulus of porous low-k SiO<sub>2</sub> xerogel films

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#### Abstract

A range of mesoporous xerogel low-k dielectric films were prepared and characterised using complementary techniques: Laser-generated surface acoustic waves, ellipsometric porosimetry, Rutherford backscattering and nanoindentation. The density, porosity, pore size distribution, cumulative surface area, elastic modulus and hardness of the films were measured as well as their dielectric constants. Dielectric constant values of k = 1.7-2.3 were measured for samples with porosities of 36–55%. Mean pore radii values of 2.2-4.2 nm and surface areas of 280-240 m<sup>3</sup> cm<sup>-3</sup> were also obtained. Using porosity and mean film density values determined using different techniques, the film skeletal density of these samples were calculated to be  $\approx 1.4$  g cm<sup>-3</sup>, almost 40% lower than that of dense SiO<sub>2</sub>. The elastic moduli of the films were found to be E < 4 GPa. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Xerogel; Thin film; Low-k dielectric; Porous; SiO<sub>2</sub>; Spin-on; Characterisation; Porosity; Elastic modulus

## 1. Introduction

As low-k materials begin to make the move into mainstream microelectronic fabrication processes, mesoporous silica has become one of the principal candidate materials capable of achieving ultra-low dielectric constant values of k < 2. While the introduction of pores into the solid material reduces its dielectric constant, it also reduces its mechanical strength. This has implications for further processing where high mechanical forces are used, e.g., during chemical mechanical polishing (CMP). A

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compromise is therefore necessary between attractive electrical properties and reduced mechanical strength resulting from high porosity.

Established techniques to characterise the density, porosity and mechanical strength of porous dielectric films vary in complexity. This paper compares results from five samples measured using non-destructive techniques which have recently been developed: laser-generated surface acoustic wave characterisation (LSAW) and ellipsometric porosimetry (EP). Density and porosity results are compared to Rutherford backscattering (RBS) data. Elastic modulus results are compared to those obtained by means of nanoindentation.

## 2. Experimental

A number of mesoporous silica films were deposited on 150 mm n-type silicon wafers using variations of a sol-gel spin-on process described elsewhere [1]. These process variations, labelled A to E, allowed the porosity to be varied and therefore the dielectric constant. After annealing to 450°C for 1 h, each film was exposed to hexamethyldisilazane (HMDS) vapour for a period of 24 h to achieve hydrophobisation of the inner pore surfaces. HMDS effectively removes the H atom from hydrophilic surface Si–OH groups and replaces them with  $-Si-(CH_3)_3$  which is less polar and hydrophobic [2]. The end effects, which are highly desirable, are that the dielectric constant *k* and leakage current density  $J_{leak}$  both decrease after HMDS treatment.

These films were then characterised using LSAW, EP, RBS and nanoindentation. The LSAW, RBS and nanoindentation work was performed on parts of the same wafer, while EP was carried out on wafers spun-on at the same time using the same precursor. These are assumed to have identical properties. The capabilities of these techniques are shown in Table 1. A complete description of each measurement technique is beyond the scope of this paper. However it is necessary to describe certain aspects of the techniques to correctly interpret the results.

A new surface acoustic wave technique, LSAW, measures the velocity dispersion of laser-generated wideband surface acoustic waves as a function of frequency as they travel through the film and substrate [3]. This dispersion depends on the properties of the layer (thickness, elastic modulus, Poisson's ratio and average film density). The large mismatch between the acoustic properties of the Si wafer substrate and the porous silica film makes this method well suited to this task. Using the measured film thickness and assuming a constant Poisson's ratio (v = 0.21 in all cases), absolute values of average film density and elastic modulus can be determined by curve fitting. Porosity can then be calculated using a value of film skeletal density  $\rho_{skeleton}$  as shown in Eq. (1). We used the

	Film thickness	Refractive index (film and skeleton)	Mean film density	Porosity	Pore size distribution	Surface area	Elastic modulus	Hardness	Atomic density
LSAW EP	•	•	•	0	•	0	•		
RBS/ERD Nanoindentation			0	0			$\odot$	$\odot$	•

Table 1 Characterisation methods and capabilities

 $\bullet$  = Proven,  $\bigcirc$  = possible,  $\bigcirc$  = proven for dense films.

simplest case of dense SiO<sub>2</sub>,  $\rho_{SiO_2} = 2.26$  g cm<sup>-3</sup>. It should be noted that dense SiO<sub>2</sub> density values vary with respect to crystalline structure or film deposition method, so it is important to specify the exact value used. The inherent accuracy of the technique is related to film thickness and average density – for these samples of the order of ±3% for porosity and ±0.5 GPa for elastic modulus. Thinner films (<200 nm) with densities close to that of the substrate reduce dispersion and therefore fitting accuracy. The distance between the wave source and piezoelectric detector can be varied in the order of 5–20 mm, so results are not point-specific. LSAW is, as far as we know, the only method which allows porosity information and mechanical properties to be gained at the same time. Another advantage of this method is that, in comparison to previous SAW methods, special patterned oscillating sensor substrates are not required so it is better adapted to serve in volume production. It is also non-destructive, requiring relatively simple setups and results can be achieved in minutes. The application of the method to multilayer systems is more complex.

$$\pi = 1 - (\rho_{\rm film} / \rho_{\rm skeleton}) \tag{1}$$

Multi-angle single frequency ( $\lambda = 632.8 \text{ nm}$ ) EP [4] measures the film refractive index  $n_{\text{film}}$  and uses a reference value of skeletal refractive index  $n_{\text{skeleton}}$  to calculate the 'full' porosity using the Lorentz-Lorenz Eq. (2). Here we used the simplest case of  $n_{\text{skeleton}} = n_{\text{SiO}_2} = 1.46$ . It also measures the change in ellipsometric characteristics  $\Delta$  and  $\Psi$  during desorption of toluene vapour and calculates the 'open' porosity, i.e., that portion of the pore network available to toluene penetration. If the full and open porosities are equal, all the pores in the film are said to be interconnected. The pore radius limit to toluene penetration is r=0.5 nm. The pore size distribution (PSD) is also calculated from ellipsometric optical constant changes during toluene desorption using the Kelvin and BET equations [4]. The *cumulative* surface area is calculated by integrating the PSD data for a cylindrical pore model. The accuracy is estimated to be  $\pm 3\%$ . This method is also non-destructive, fast and can be applied to multilayers with known optical characteristics. Mechanical characteristics such as elastic modulus are not available using EP.

$$\pi = 1 - \left[ (n_{\text{film}}^2 - 1)/(n_{\text{film}}^2 + 2) \right] / \left[ (n_{\text{skeleton}}^2 - 1)/(n_{\text{skeleton}}^2 + 2) \right]$$
(2)

RBS allows the absolute measurement of atomic concentrations of an element with a sensitivity proportional to the atomic mass difference between the element in question and the matrix it is situated in [5]. For porous samples, the atomic density is measured and mean film density or equivalent dense thickness can be calculated using dense SiO<sub>2</sub> reference sample results. The porosity is simply calculated using the measured and equivalent dense values of density or thickness. An estimated accuracy of  $\pm 5\%$  includes inherent RBS errors and also film thickness variations around the wafer. Of particular interest for these films are the concentrations Si, O and C. Elastic recoil detection (ERD) can be employed to detect lighter elements such as F and H concentrations for example [6]. This method is impractical for in-line control due to complex experimental requirements.

In the nanoindentation technique, a known force is applied to a geometrically-shaped indenter which is driven into the film sample to a measurable depth [7]. Using analytic or finite element modelling, some of the material mechanical properties can be derived from the indentation load-displacement data. Porosity information is not available using nanoindentation. The accuracy depends

on film thickness, film structure and the mismatch between film and substrate elastic constants. Despite the relative complexity involved in interpreting the results, this method is becoming widely used in the industry.

The electrical characteristics of the films were measured using an SSM CV 495 Hg probe system. Some samples were deposited on highly doped wafers ( $<4 \text{ m}\Omega \text{ cm}$ ) to prevent parasitic capacitances during measurement. The wafer dopant concentration is assumed to play no role in the determination of non-electrical characteristics. Film thicknesses were measured using profilometry and variable angle spectroscopic ellipsometry (VASE).

# 3. Results

The thickness, dielectric constant, LSAW mean film density, RBS  $[SiO_2]$  concentration and porosity values are shown in Table 2 and Fig. 1. *k* clearly decreases with increasing porosity as expected. However the porosity values themselves vary between the three techniques. LSAW values are about 5% higher than RBS, and EP about 12–20% less than RBS.

LSAW and RBS porosity values correlate well with each other. To calculate porosity  $\pi$ , a reference density value for the film skeleton material must be used as shown in Eq. (1). Therefore the question of reference density becomes very important. An absolute value measured by RBS on a 490 nm thick thermally-grown dense SiO<sub>2</sub> film was 2.24 g cm<sup>-3</sup>±5%. This closely matches the published [8] tridymite SiO<sub>2</sub> density value of  $\rho = 2.26$  g cm<sup>-3</sup>. In the LSAW and RBS calculations, these typical dense reference values were used. However, the real skeletal material density may be much lower. The film skeleton contains C, H and F from the sol–gel process which may significantly reduce the skeletal density. For example, inclusion of up to 10–12 at.% F in CVD SiO<sub>2</sub> leads to a density reduction of about 5% [9]. It is also known that C concentrations of 18–30 at.% can reduce SiO<sub>2</sub> density to values of 1.3–1.5 g cm<sup>-3</sup> in CVD low-*k* films [10]. RBS/ERD results on a similar non-HMDS treated xerogel sample indicate an atomic film composition of SiO<sub>2</sub>F<sub>0.2</sub>C<sub>0.1</sub>. These small concentrations of F and C are unlikely to cause a massive reduction in SiO<sub>2</sub> density if such a material

Table 2 Film thickness, dielectric constant, LSAW and RBS results

Process	$t^{a}$ (nm) $\pm 3\%$	k <sup>ь</sup> ±0.1%	LSAW $\rho_{\text{film}}$ (g cm <sup>-3</sup> ) ±3%	LSAW <sup>c</sup> $\pi$ (%) ±3%	RBS [SiO <sub>2</sub> ] $(10^{22} \text{ cm}^{-3})$ ±5%	$\begin{array}{c} \text{RBS}^{\text{d}} \\ \pi \\ (\%) \\ \pm 5\% \end{array}$	EP full <sup>e</sup> $\pi$ (%) ±3%	EP open $\pi$ (%) $\pm 3\%$
A	461	2.3	0.89	61	3.0	57	35	36
В	469	2.3	0.87	61	3.0	56	38	40
С	567	2.1	0.72	68	2.5	64	50	51
D	632	1.9	0.65	71	2.1	67	54	55
E	544	1.7	0.65	71	2.2	68	52	54

<sup>a</sup> Measured by white light interference, mean of 10 points per wafer.

<sup>b</sup> Calculated using profilometry thickness measurements at the CV measurement point.

<sup>c</sup> Calculated using reference  $\rho(\text{SiO}_2) = 2.26 \text{ g cm}^{-3}$ .

<sup>d</sup> Referenced to an RBS measured 490 nm thick dense thermal oxide  $\rho(SiO_2) = 2.24$  g cm<sup>-3</sup>.

<sup>e</sup> Measured by multiangle ellipsometry and calculated using reference  $n_{(SiO_2)} = 1.46$  in the Lorentz–Lorenz equation.



Fig. 1. Porosity and k values.

was deposited by CVD. However, the inherent fractal structure of the sol-gel produced skeletal material is likely to be much less dense than a corresponding CVD film. Recent SXR/SANS (specular x-ray reflectivity/small-angle neutron scattering) experiments [11] carried out on the porous low-*k* dielectric material Nanoglass<sup>TM</sup> indicate a skeletal density of  $1.16\pm0.05$  g cm<sup>-3</sup> for a sample of composition SiO<sub>1.8</sub>C<sub>0.7</sub>H<sub>1.7</sub>. The carbon concentration consisted of both organic groups remaining from the precursor residing in the skeleton, and also methyl groups introduced to the pore surfaces during hydrophobisation and are therefore similar to the films described in this work. Therefore it is likely that the real skeleton density of the films described here are much lower than that of dense SiO<sub>2</sub> and thus the porosity values calculated for LSAW and RBS are too high.

EP results produced values of open and full porosity for all samples to within experimental error of each other, suggesting that the pore networks were completely interconnected. Measurement of refractive index *n* performed during EP and separately using VASE are in good agreement as shown in Fig. 2. While full porosity is calculated using a skeletal reference refractive index of dense  $SiO_2$ , open porosity does not use dense  $SiO_2$  reference values in its calculations. Using the EP open porosity and



Fig. 2. n vs. open porosity.

Process	EP open (%) ±3%	LSAW $ ho_{\text{skeleton}}$ (g cm <sup>-3</sup> ) $\pm 6\%$
A	36	1.39
В	40	1.46
С	51	1.46
D	55	1.44
E	54	1.41

Table 3Skeletal density calculations

the mean film density obtained by LSAW, the skeletal density was calculated (Table 3). The values lie in the range 1.39-1.46 g cm<sup>-3</sup>, and are therefore about 40% lower then dense SiO<sub>2</sub>, but higher than that measured for Nanoglass [11]. This result suggests that the skeletal refractive index might also be different to that of SiO<sub>2</sub>. However the full and open porosity values match closely.

Further VASE investigations indicate a quite significant change in n and film thickness during processing, as shown in Fig. 3. The film thickness shrinks by 5% after annealing and then expands back to near its original value after HMDS treatment. The refractive index increases by 4% after HMDS treatment. An increase of not more than 1% in refractive index is expected due to pore volume reduction after HMDS treatment. As hydrogen bonded water is also replaced during the reaction of HMDS with surface hydroxyl groups, the remaining contribution to n is probably due to the slightly higher refractive index of HMDS compared to water, shown in Table 4.

The mean pore radii and surface area of each sample obtained by EP are shown in Fig. 4. The mean pore radius increases with increasing sample density from 2.2 to 4.2 nm. However, the surface area decreases somewhat, from 280 to 240 m<sup>2</sup> cm<sup>-3</sup> indicating that while the pores are larger at higher porosities, there are fewer of them. This is common to such films [12].

The mechanical characteristics of the films are shown in Fig. 5. Overall the elastic modulus and hardness values are comparatively low – we have previously achieved values of 5 GPa and higher



Fig. 3. *n* and *t* during processing.

Table 4 Refractive index n of various materials

Material	n
SiO <sub>2</sub>	1.45
HMDS	1.41
Water	1.33



Fig. 4. Surface area and mean pore radius vs. open porosity.

measured by LSAW for samples produced using a slightly different process. The nanoindentation elastic modulus values are at least twice those reported by LSAW on the same samples. The reason for this is due to uncertainties resulting from substrate effects. When the substrate and film have significantly different elastic moduli, results with an error of <20% can be guaranteed only with films of thickness  $\approx 1 \ \mu m$ , and then only if the indent penetrates <10% of the thickness of the film. The indent tests performed on these  $\approx 0.5 \ \mu m$  thick films penetrated 10% of the film thickness, leading to



Fig. 5. E-modulus and hardness vs. open porosity.

a probable over-estimation of >20% in elastic modulus values. Another unknown factor is the possible densification of material under the nanoindenter tip which adds to measurement error. The maximum error in the LSAW calculated E moduli are estimated to be  $\approx \pm 0.5$  GPa for the thinnest films, or 35–80% for these low modulus values. For a film of thickness of 1 µm, the error reduces to about  $\pm 10\%$ .

# 4. Conclusions

The techniques employed in this study demonstrate considerable ability and usefulness in characterising low-k mesoporous silica xerogel films. The choice of reference film skeletal density and refractive index used in calculations plays a large role in the determination of porosity, and reference values from dense SiO<sub>2</sub> cannot be assumed to return accurate results. The EP full and open porosities were similar, suggesting the pore network is completely open, and were somewhat low for films with these dielectric constants. Combining EP open porosity and LSAW mean film density allows the calculation of skeletal density. Given that the density of the skeleton appears to be 40% lower than that of SiO<sub>2</sub>, the validity of using  $n_{skeleton} = n_{SiO_2}$  in Eq. (2) must also be questionable. If  $n_{skeleton} \neq 1.46$  before HMDS treatment, the treatment will change the measured  $n_{film}$ , and so the calculated full porosity. More work is required to investigate the extent of this effect.

The elastic moduli of the films measured using LSAW and nanoindentation displayed similar trends, but were low at 0.6 < E < 4 GPa for all films. The likely overestimation of the nanoindentation results was due to substrate effects. While LSAW claims better accuracy for  $\approx 1 \ \mu m$  thick films than nanoindentation, both techniques demonstrate the continuing challenges which need to be overcome to obtain accurate elastic modulus results for  $\approx 0.5 \ \mu m$  films. These techniques will refine themselves as the sample database grows.

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