Paper

Ellipsometric spectroscopy studies of compaction and decompaction of Si-SiO$_2$ systems

Witold Rzodkiewicz and Andrzej Panas

Abstract— The influence of the strain on the optical properties of Si-SiO$_2$ system has been investigated by spectroscopic ellipsometry (SE), interferometry and weighing methods. Subtle changes of densification (compaction degree) in silicon dioxide layers on silicon substrates have been determined by weight technique (relying on measurements of the silicon dioxide layer mass and calculations of the volume). Elastic stress in the oxide layers has been measured by Fizeau fringes image analysis method. A comparison is made between the density of the silicon dioxide (ρ) and the results of calculations made using $\rho = f(n)$ relations (where n is the refractive index) given in the literature.

Keywords— Si-SiO$_2$ system, density, refractive index, spectroscopic ellipsometry.

1. Introduction

Oxidation of silicon has attracted much attention in the last decades. Due to the continuous miniaturization of integrated circuits and increased functionality in the modern microelectronics technology, better understanding of the mechanisms of elastic (instantaneous and reversible compaction) and non-elastic (irreversible and permanent densification) strain generation in the Si-SiO$_2$ system is necessary. Furthermore, when the structure size is reduced, their mechanical and optical properties may differ from the corresponding values of the bulk medium. Therefore, studies of both mechanical and optical properties of Si-SiO$_2$ system are of great importance.

Several methods, such as spectroscopic ellipsometry (SE), interferometry and weight technique (WT) have been used to determine these properties. In connection with this, the main goal of our work was to study the influence of strain on the optical properties of Si-SiO$_2$ system using the techniques mentioned above.

2. Experimental characteristics

Czochralski-grown, n-type (100) silicon substrates have been used in this study. We started with 4-inch wafers polished on both sides. Subsequently, the wafers were subjected to thermal oxidation process at 1000°C in either dry oxygen (in order to grow silicon dioxide layers with the thickness of approximately 45, 95, and 170 nm) or water vapor (in order to grow oxide layers with the thickness of approximately 50, 90, and 165 nm).

The thickness of SiO$_2$ layers formed in the way described above and their refractive indexes were determined using a variable angle spectroscopic ellipsometer (VASE) of J. A. Woollam Inc. Co.

Ellipsometric measurements were carried out at 5 points for each wafer in a wide spectral range (250–1000 nm) at three angles of incidence (65°; 70°; 75°). Interferometry was used to determine the radius of curvature of the investigated wafers.

2.1. Experiment methodology

The sequence of processing and measurement steps performed during our investigations was as follows:

1. Oxidation of 4-inch, n-type Si (100) wafers polished on both sides.
2. Interferometric measurements of oxidized wafers.
3. Ellipsometric measurements of oxidized wafers (to determine the thickness and refractive index of oxide).
4. Measurements of the mass of oxidized wafers.
5. The removal of both front-side SiO$_2$ layer and back-side SiO$_2$ layer of each wafer by etching in HF solution.
6. Measurements of the mass of as-etched wafers.
7. Interferometric measurements of as-etched wafers.
8. Calculations of the oxide mass as the difference between the wafer mass obtained before and after removal of both front-side and back-side oxide.
9. Calculations of oxide density as the ratio of the determined oxide mass to its calculated volume (product of oxide thickness and the surface area).

2.2. Optical model for ellipsometric data analysis

The optical model which used for spectro-ellipsometric data analysis consisted of a silicon dioxide layer and a silicon substrate. The Cauchy dispersive model enabled the silicon dioxide refractive index and its thickness to be determined. Determination of the SiO$_2$ index of refraction is based on the he relationship represented by the Cauchy dispersion formula:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots, \qquad (1)$$

where A, B, C are fitting coefficients, and λ stands for wavelength, expressed in μm. In the applied model, the three parameters of Eq. (1) and SiO$_2$ layer thickness were fitted.

3. Results and discussion

Dependence of silicon dioxide density, ρ_{ox} on the oxide refractive index n is illustrated in Fig. 1. This figure clearly shows that the refractive index is a measure of the densification degree of SiO$_2$ layers on silicon substrates. The measurement and calculation results for wafers with silicon dioxide thickness $t_{ox} \approx 50$ nm, 90 nm, 170 nm are presented in Tables 1–4.

Once the mass $M_{\mathrm{SiO_2}}$ of an SiO$_2$ layer is measured and its volume $V_{\mathrm{SiO_2}}$ is known (calculated as the product of the oxide thickness and surface area of the layer), one may determine directly the density of the layer:

$$\rho_{\mathrm{SiO_2}} = \frac{M_{\mathrm{SiO_2}}}{V_{\mathrm{SiO_2}}}. \qquad (2)$$

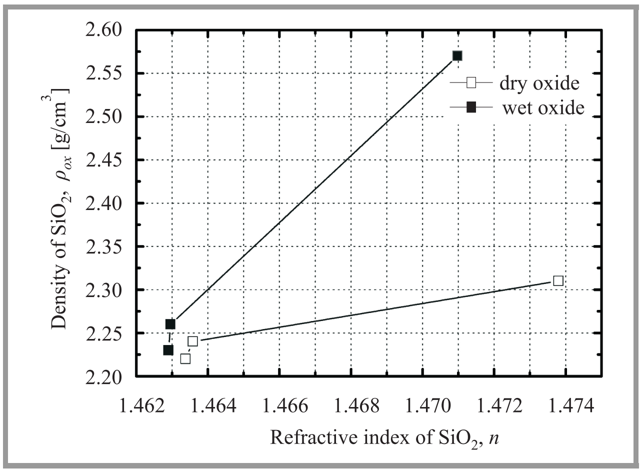

Fig. 1. Dependence of silicon dioxide density, $\rho_{\mathrm{SiO_2}}$ (experimentally determined by weight technique) on the oxide refractive index, n (determined by spectroscopic ellipsometry).

Table 1
The mass, density and averaged thickness values determined for silicon wafers oxidized in water vapor atmosphere

No. of wafer	t_{ox} [nm]	M_{ox} [mg]	ρ_{ox} [g/cm^3]
1	50.07	1.00	2.57
2	90.17	1.58	2.26
3	165.12	2.86	2.23

Table 2
The mass, density and averaged thickness values determined for silicon wafers oxidized in dry atmosphere

No. of wafer	t_{ox} [nm]	M_{ox} [mg]	ρ_{ox} [g/cm^3]
4	45.16	0.81	2.31
5	93.96	1.64	2.24
6	172.02	2.97	2.22

Table 3
Comparative collection of theoretical and experimental density values determined for the corresponding averaged refractive indexes (determined by SE at $\lambda = 630$ nm) of the wet oxides (oxides grown in water vapor)

No. of wafer	n_{630}	$\rho_{L\text{-}L}$	$\rho_{G\text{-}D}$	ρ_{Ta}	ρ_{Eyk}	ρ_{Drude}	ρ_{wt}
		[g/cm^3]					
1	1.4710	2.25	2.25	2.29	2.25	2.26	2.57
2	1.4630	2.21	2.22	2.23	2.21	2.22	2.26
3	1.4629	2.21	2.22	2.23	2.21	2.22	2.23

Table 4
Comparative collection of theoretical and experimental density values determined for the corresponding averaged refractive indexes (determined by SE at $\lambda = 630$ nm) of the dry oxides (oxides grown in dry oxygen)

No. of wafer	n_{630}	$\rho_{L\text{-}L}$	$\rho_{G\text{-}D}$	ρ_{Ta}	ρ_{Eyk}	ρ_{Drude}	ρ_{wt}
		[g/cm^3]					
4	1.4738	2.26	2.27	2.31	2.26	2.28	2.31
5	1.4636	2.21	2.22	2.23	2.22	2.22	2.24
6	1.4634	2.21	2.22	2.23	2.22	2.22	2.22

Next, the density of SiO$_2$ layers obtained in this way were compared with that determined from the value of the refractive index (established in the course of ellipsometric measurements). The Lorentz-Lorenz equation [1, 2] (L-L) is one of the most widely used formulae relating oxide density to its refractive index:

$$\Pi = \frac{1}{3} \mathrm{N_A} \alpha = \frac{(n^2-1)}{(n^2+2)} \frac{M}{\rho}, \qquad (3)$$

where: Π – molar polarization, $\mathrm{N_A}$ – Avogadro's number, α – mean polarizibility, M – molecular mass, ρ – density.

Substituting the following values: $M = 60.08$ g/mol (molecular mass of SiO$_2$), $\rho = 2.2$ g/cm^3 and $n = 1.46$ (density and refractive index of the relaxed SiO$_2$, respectively), we obtain molar polarization for SiO$_2$ layer $\Pi = 7.4797$ cm^3/mol and Eq. (1) becomes:

$$\rho = 8.0324 \frac{n^2-1}{n^2+2}. \qquad (4)$$

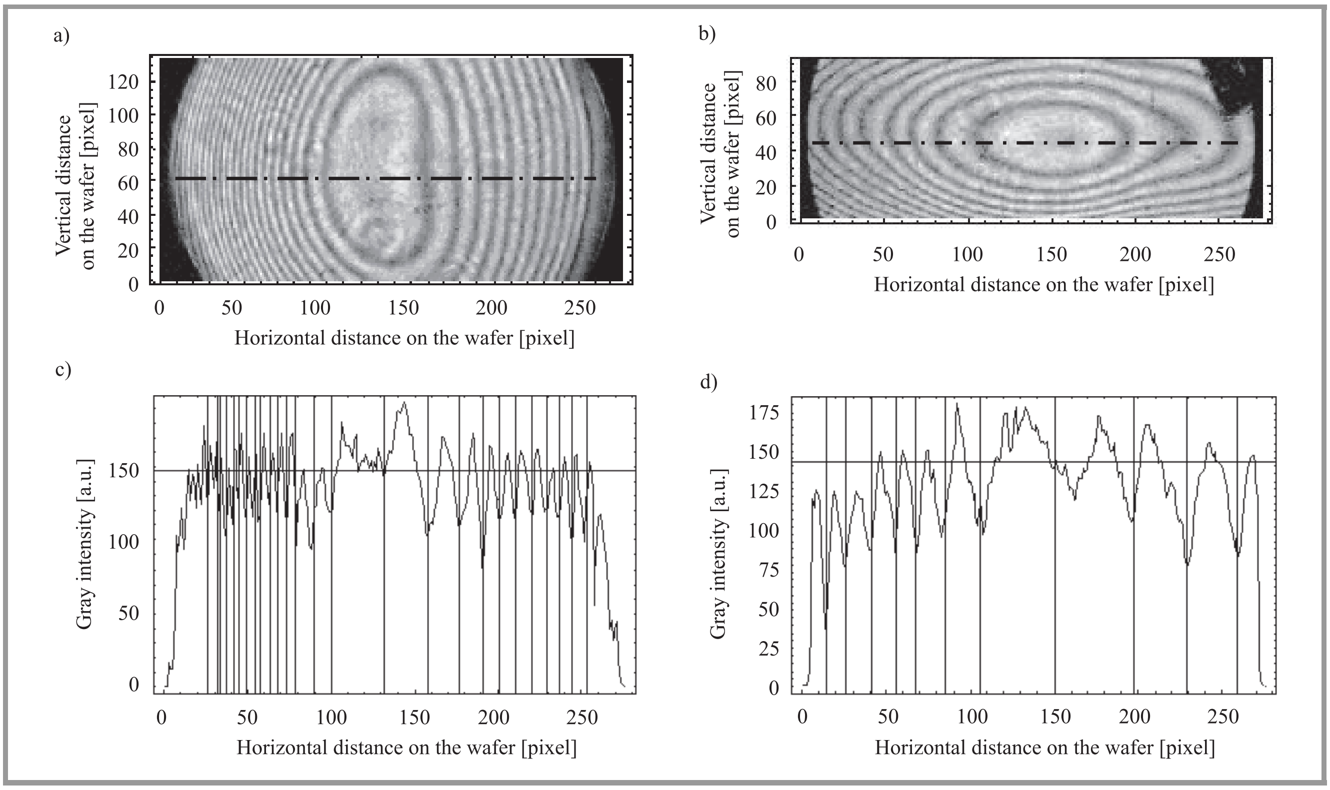

Fig. 2. Interferograms and theirs sections along horizontal axis and the center of Fizeau fringes for front-side (a), (c) and back-side (b), (d), of wafer no. 5 after dry oxidation.

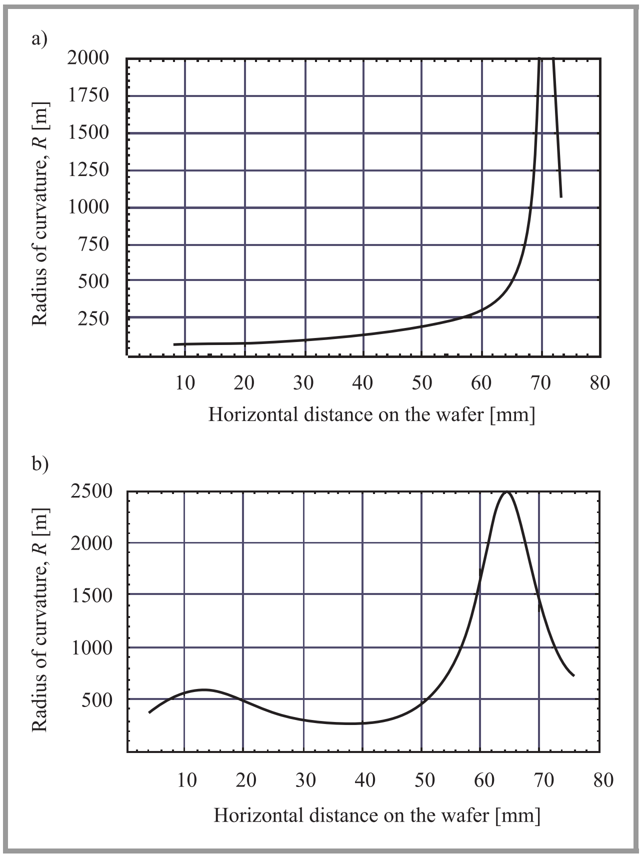

Fig. 3. Radius of curvature versus distance for front-side (a) and back-side (b) of wafer no. 5 after dry oxidation.

Other models of the relationship between oxide density and its refractive index include: Gladstone-Dale formula [2, 3] (G-D):

$$\rho = 4.785\, n - 4.784\,, \tag{5}$$

the empirical $\rho(n)$ relationship for SiO_2 layer derived by Taniguchi [4] (Ta):

$$\rho = 7.81\,(n-1)^{1.63}, \tag{6}$$

Eykman equation [5] (Eyk):

$$\rho = C\,\frac{n^2-1}{n^2+0.4}\,, \tag{7}$$

where $C = 3.6161$ (at room temperature) – empirical constant dependent on temperature; and Drude equation [2]:

$$\rho = 1.944\,(n^2-1)\,. \tag{8}$$

The last two equations have usually been used to study the optical properties of various liquids (such as chlorobenzene, methanol, water, etc.).

A comparison between values of SiO_2 density obtained both experimentally and theoretically is shown in Tables 3 and 4. It should be noticed that the results obtained for dry oxides by means of WT and calculated using Eq. (5) are in a good agreement (see Table 4).

The results of interferometric measurements are illustrated in Figs. 2–5. Interferograms and theirs sections along horizontal axis and the center of Fizeau fringes for front-side

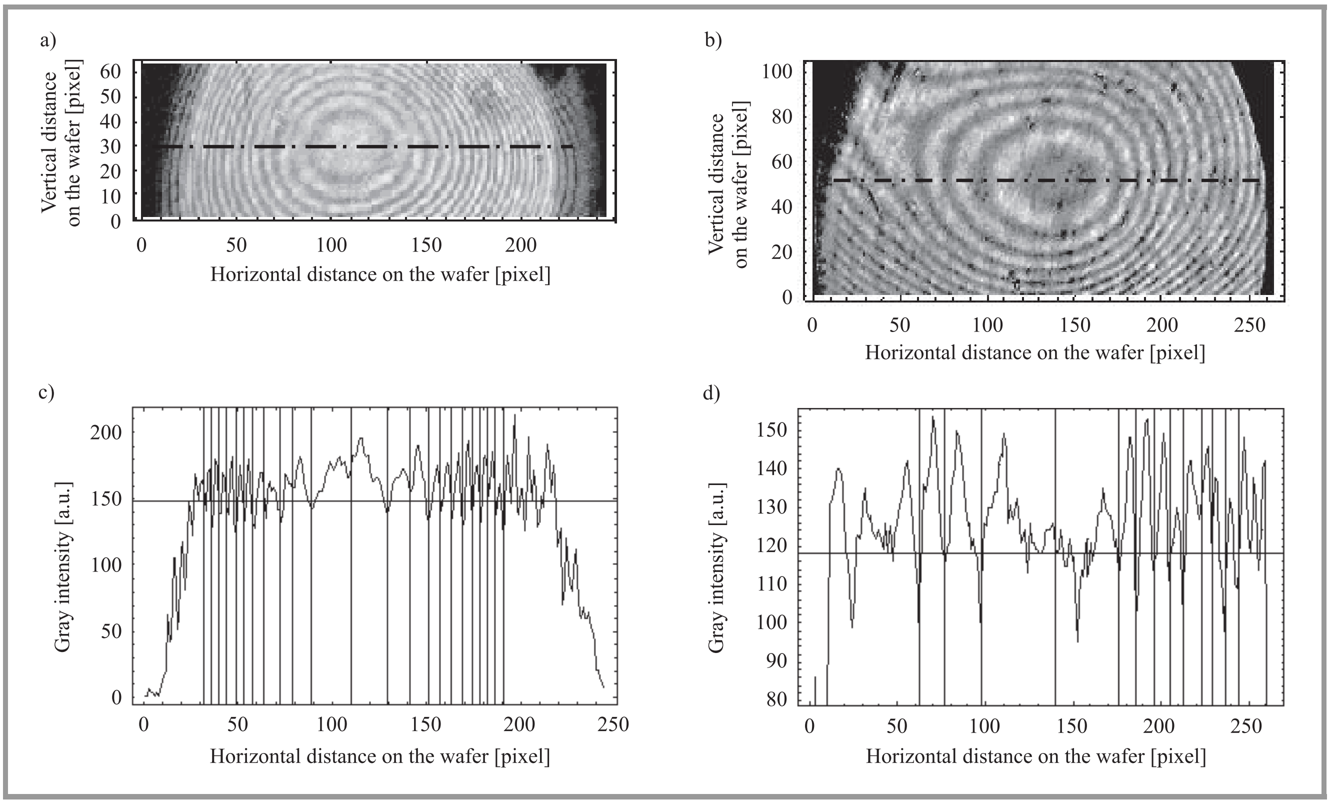

Fig. 4. Interferograms and theirs sections along horizontal axis and the center of Fizeau fringes for front-side (a), (c) and back-side (b), (d), of wafer no. 5 after removal of dry oxide.

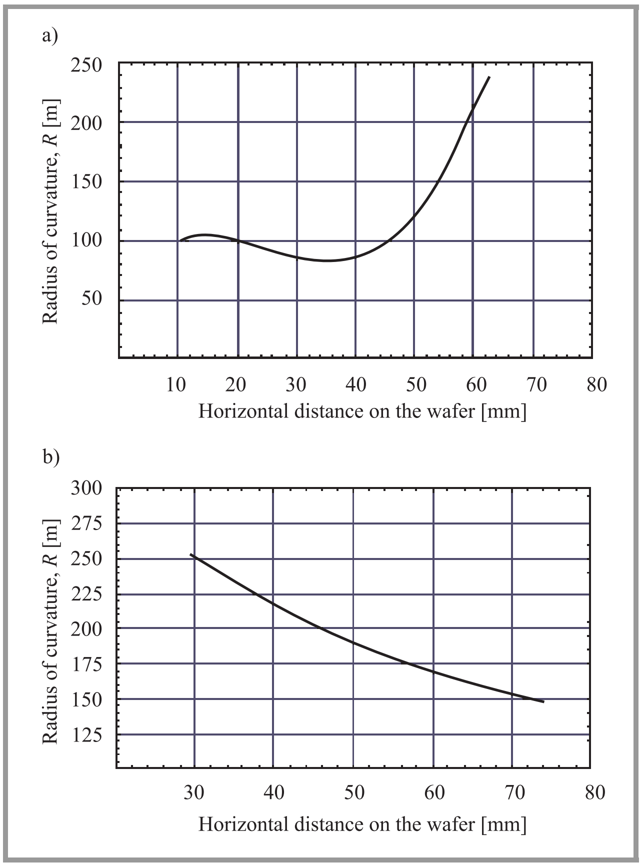

Fig. 5. Radius of curvature versus distance for front-side (a) and back-side (b) of wafer no. 5 after removal of dry oxide.

and back-side of wafer no. 5 after dry oxidation (thickness of ~ 90 nm) are shown in Fig. 2. Similar data obtained after removal of thick dry oxide is presented in Fig. 4.

Using the results shown in Figs. 2 and 4, the approximation function of curve of the sections, as well as the corresponding formula for reciprocal curvature Eq. (9), we have determined the radius of curvature R versus distance for front-side and back-side of the oxidized wafer (dry SiO$_2$ thickness of ~ 90 nm) (see Fig. 3):

$$R = \frac{1}{\kappa} = \frac{\left[1 + \left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2\right]^{\frac{3}{2}}}{\frac{\mathrm{d}^2 y}{\mathrm{d}x^2}}, \tag{9}$$

where κ is the curvature.

Similar results are shown in Fig. 5 for front-side and back-side of the wafer after dry oxide removal.

Comparison of the results obtained from wafer no. 5 after oxidation and after etching indicates that the curvature of an oxidized wafer is considerably smaller than that of an etched wafer (Figs. 3 and 5).

4. Conclusions

In this work, we have investigated the influence of strain on the optical properties of Si-SiO$_2$ system by spectroscopic ellipsometry and interferometry.

On the basis of the obtained results, we have drawn the following conclusions:

- refractive index of wet oxide is lower than that of dry oxide (Tables 3 and 4);
- for refractive index higher than 1.47, the divergence between the density calculated from the Taniguchi formula and that calculated from Lorentz-Lorenz, Gladstone-Dale, Eykman, and Drude equations becomes significant (Tables 3 and 4);
- measurement of oxide mass and calculated volume of the oxide layer enabled the densification degree of the oxide layers on silicon substrates to be properly determined for about 83% of the investigated wafers (with numbers: 2–6);
- the local radii of curvature of oxidized wafer no. 5 are considerably higher than those of the etched wafers (Figs. 3 and 5);
- interferometry and spectroscopic ellipsometry have turned out to be helpful and suitable methods in our studies.

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