Nanometer-scale depth-resolved atomic layer deposited SiO$_2$ thin films analysed by glow discharge optical emission spectroscopy

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In this contribution, pulsed radio frequency (rf) glow discharge optical emission spectroscopy (GDOES) was used to investigate the film properties of SiO$_2$ deposited by plasma enhanced atomic layer deposition (PEALD), *e.g.* the chemical composition, structural properties and film thickness. The total sputtering time until the interface between the SiO$_2$ layer and the Si substrate was ~13 s. The main impurities in the film, *i.e.* H, C and N, were detected. We observed that both C and N intensities decreased with increasing plasma power applied during deposition of the thin film, suggesting that a higher plasma power increases the reactivity of the PEALD process and thus decreases the concentration of impurities in the deposited film. Moreover, the deviation of the GDOES sputtering rates on the film were related to the film density. The thickness of one-hundred-nanometer range SiO$_2$ film was calculated from the GDOES silicon and oxygen emission profiles, and its difference from ellipsometry and X-ray reflectivity measurements highlights the challenges for the GDOES technique for transparent thin films.

1 Introduction The layer-by-layer growth mechanism of atomic layer deposition (ALD) leads to several unique advantages over other techniques such as plasma enhanced chemical vapor deposition (PECVD) and physical vapor deposition (PVD), *e.g.* precise film thickness control, high uniformity and superb conformality. In addition, in order to broaden the thin film properties processing prospects, a plasma-enhanced ALD (PEALD) method can be applied. The growth mechanism and properties of PEALD films are usually dependent on the reaction conditions such as plasma power, pulse time and temperature [1]. The determination of an effective characterization method is thus needed to understand the influence of process parameters.

Radio-frequency glow discharge optical emission spectroscopy (rf-GDOES) has been applied for diverse thin film analyses, both on insulating and conducting layers. It has been used *e.g.* for the analysis of PECVD SiO$_2$ layers [2–4], PVD Cu(In,Ga)Se$_2$ thin film [5] and atomic layer deposition (ALD) ZnO [6]. Most of the work has focused on the elemental concentration profiles and the development of the novel instrumental setups. However, expanding the application domains of GDOES requires further investigation to improve interpretation of the measured film properties.

The analytical capabilities of rf-GDOES instruments have seen significant advancement in recent years [7]. Compared to other analytical techniques, such as secondary ion mass spectrometry (SIMS) or elastic recoil detection analysis (ERDA), rf-GDOES has the advantages of high sputtering rate and throughput, short specimen preparation time, high analytical depth (several nm to ~100 μm), and large analysis area [5]. In addition, the use of a pulsed source has increased depth resolution, now down to the nanometer scale.

In the present contribution, we thus studied the applicability of GDOES analyses for SiO$_2$ thin films deposited by PEALD at low temperature. To evaluate the impact of plasma power on ALD film, we studied the chemical composition, quality and thickness of PEALD SiO$_2$ films.

2 Experimental PEALD SiO$_2$ films deposited on (100)-oriented Czochralski silicon substrates from

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bis(tertiary-butylamino)silane (BTBAS) and O_2 plasma with different powers (50, 180 and 300 W) were analysed in this study. All depositions were done a with Beneq TFS 200 ALD-reactor using a capacitively coupled plasma source at 90 °C.

The samples were analysed with a Horiba GD-Profiler 2 rf-GDOES instrument. A 4-mm diameter anode and rf-power at 35 W (*i.e.*, low power conditions) in pulsed mode were used. Pre-flushing (Ar) and low-power surface cleaning were used to minimize the impact of surface contamination. The spectral information was acquired as intensity *vs.* time profile of the characteristic emission line of each element. The emission profiles were qualitatively analysed and compared among the different samples, due to the lack of reference samples to allow for quantification of the concentrations. For thin film thickness, measurements of ellipsometry and X-ray reflectivity (XRR) were performed. A SENTECH SE400adv ellipsometer was used at 632.8 nm wavelength and 70° angle of incidence, and a Phillips X´Pert Pro X-ray diffractometer was used with Cu-K$_{\alpha1}$ radiation. The measured XRR data was then simulated with a software using Parratt's formalism [8] in order to obtain thickness and density of the thin films. Moreover, the thin films sputtering rate by GDOES was calculated as the ratio of film thickness measured by ellipsometry over film sputtering time. The latter was defined at 50 % height of maximum peak for the O line.

3 Results and discussion

3.1 Elemental analysis The qualitative intensities of both the O and Si emission lines are shown in Fig. 1a for the thin film deposited at 180 W plasma power. The other films presented similar O and Si profiles. Approximately four intensity oscillations in the O line and one oscillation in the Si line can be seen. The oscillations are due to the contribution to the emission from the Si substrate surface [4], which occurs when a transparent layer is deposited on a reflecting surface [9]. In addition, the increase in the amplitude of the oscillations in the lines during the sputtering process is due to the layer becoming thinner [9], due to the effect of a difference in the emission rates from the two matrices. Consequently, the quantification of the O concentration in the layers is hampered. Nevertheless, since the Si substrates had similar surface roughness and impurity concentrations prior to the deposition of the PEALD SiO_2 thin film, a qualitative comparison among the samples is possible. The transition from the SiO_2 thin film to the Si substrate is clear at ~ 13 s sputtering time, and it is mostly evident in the O line.

Note that the transition at the interface is rather sharp and it was evaluated to be within the accuracy of a mechanical profilometer (in the range of ± 5 nm). Additionally, based on the Si and O emission profiles, we studied the possibility to measure the film thickness by GDOES, as shown in section 3.3.
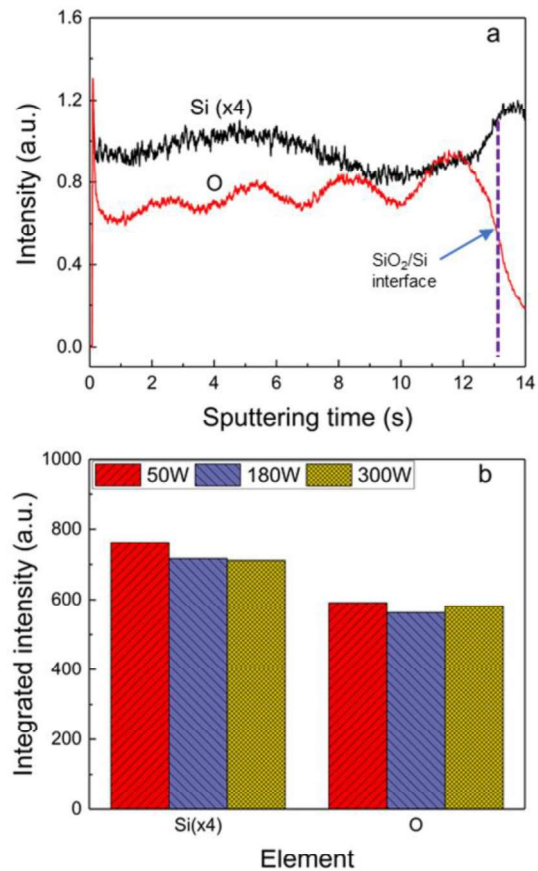
Figure 1 Example of Si and O emission profiles (a) and integrated concentrations (b) for the PEALD SiO_2 thin film deposited at 180 W. The layer transition occurs at approximately 13 s of sputtering and is shown as visual aid added in (a).

The measured emission intensity (Fig. 1b) was integrated over the whole layer thickness, where the time at the SiO_2/Si interface transition is calculated at 50% of the maximum height. Note that the reported values are not calibrated for compositional depth profiling, *i.e.* the element-dependent emission rate is not considered and thus the reported intensities of the given element can be compared among different samples, but comparison among different elements is not feasible. As we expected, the plasma power did not influence the Si intensity, *i.e.* the possible differences among the SiO_2 matrices do not lead to a significant change in the Si emission rates.

The main impurities in the film, *i.e.* H, C and N, were also detected and the emission profiles and integrated intensities are presented in Fig. 2a and 2b, respectively. Similarly to the Si and O emission profiles, also the H, C and N profiles are reported only for the film deposited at 180 W. Although the higher emission intensity for C and H at the beginning of the sputtering is a known surface effect [10], their qualitative evaluation allows for an analytical comparison between the different samples (Fig. 2b).
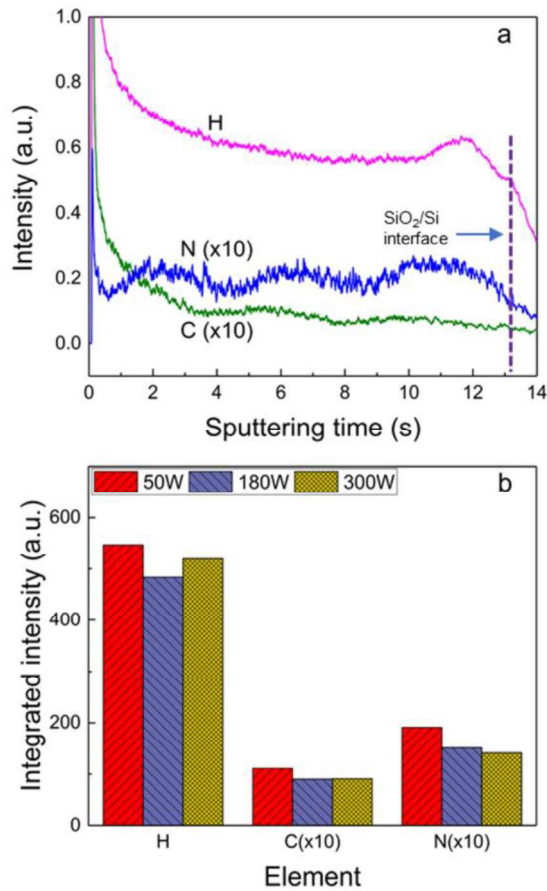
Figure 2 Example of H, C and N emission profiles (a) and integrated concentrations (b) for the PEALD SiO₂ thin film deposited at 180 W. The layer transition occurs at approximately 13 s of sputtering and is shown as visual aid added in (a), as calculated from the O profile in Fig. 1.

The hydrogen content was mostly contributed as OH-groups in the films [1,11]. Also, the emission intensity change of H among the three SiO₂ films was within the accuracy of the GDOES method, which was estimated to be within ±15%. Furthermore, there is an identifiable effect of plasma power on the film impurity levels of C and N. The intensity of the analytes seems to decrease when the set plasma power increases enough (≥180 W). This suggests that the high power can promote the completion of surface reactions while reducing film impurities due to the high plasma reactivity in the ALD process, similarly to what observed by Langereis *et al.* [12].

In addition to the GDOES profiles, Fourier transform infrared spectroscopy (FTIR) spectra were also collected. However, both the spectral and the intensity resolution did not allow to observe significant differences among the samples, *e.g.* on Si-O-Si stretching bonds or CH deformation [13].

3.2 Structural properties The sputtering time was calculated at 50% height of the peak in the O line. A slight deviation in total sputtering time was observed among the three samples, *i.e.* 12.7 s for 50 W and 13.2 s for both 180 W and 300 W. This deviation could be related either to film thickness or to film density. The former was excluded by measuring ellipsometry and XRR (which were in good agreement with each other, as shown in Table 1). Since the measurements showed almost identical film thicknesses among the samples, the deviation in the sputtering time was expected to be due to differences in the film density. The film density was measured independently by XRR. The results showed a clear density increase of the films from 1.9 to 2.2 g·cm⁻³ with increased PEALD plasma power from 50 W to 300 W. From Fig. 3, we can see that the sputtering rate decreases with increasing PEALD plasma power, and is thus likely influenced by the film density.

3.3 Film thickness calculation In addition to the elemental composition and quality of the SiO₂ films, the rf-GDOES was also used to evaluate the accuracy of measurement by studying the film thickness in a hundred-nanometer range. The sputtered film thickness, t, was calculated from the emission lines of oxygen (130 nm) and silicon (288 nm) as [9]:

$$t_i = \frac{\lambda_i}{2 n_i} \times k_i = m \times k_i \qquad (1)$$

where k is the number of oscillations in the emission intensity *vs.* time profile of the given element i, λ is the wavelength of the emission line and n is the refractive index of

Table 1 Thickness of the PEALD SiO₂ thin film deposited on Si wafers, determined by ellipsometry and XRR.

Thin film thickness (nm)	PEALD plasma power		
	50 W	180 W	300 W
Measured by ellipsometry	148 ± 0.2	146 ± 0.2	145 ± 0.2
Measured by XRR	148 ± 0.5	147 ± 0.5	147 ± 0.5
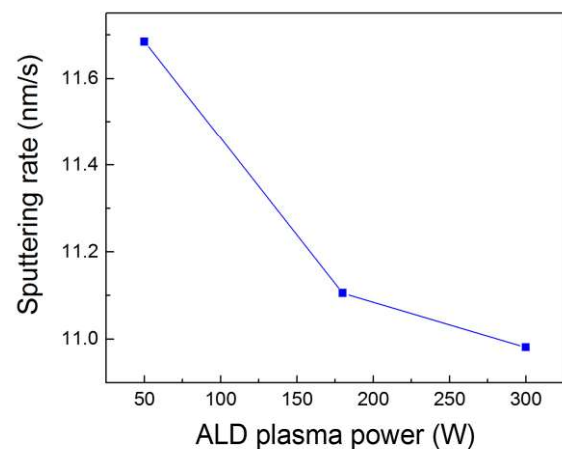
Figure 3 Sputtering rate as a function of PEALD plasma power.
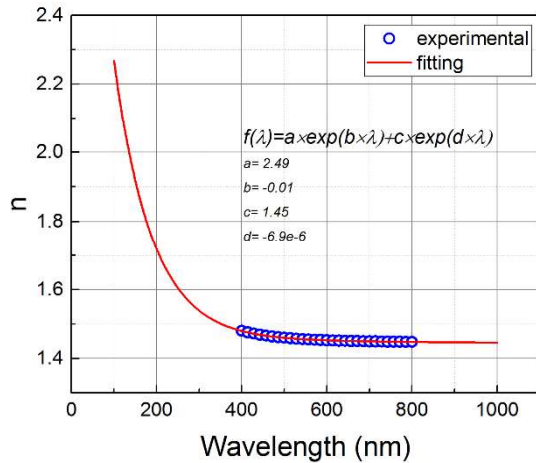
Figure 4 Simulated refractive index dispersion for the thin film deposited at 180 W. Simulation from the values measured in the visible range.

Table 2 The calculated number of oscillations k_i and simulated values of refractive index n_i with different plasma powers.

$SiO_2 - k_i, n_i$	PEALD plasma power		
	50W	180W	300W
k_O	4	4	4
k_{Si}	1.38	1.38	1.37
n_O	2.02	2.04	2.03
n_{Si}	1.55	1.55	1.56

Table 3 Calculated thickness t of SiO2 layer deposited on a silicon wafer determined from rf-GDOES emission lines (both O and Si lines).

Calculated thickness (nm)	PEALD plasma power		
	50W	180W	300W
t_O from O line	129	128	128
t_{Si} from Si line	129	128	127

SiO$_2$ at the given wavelength. The value of k was determined by fitting the emission curves to a sine curve with a linear baseline. The measurement of the refractive index in the deep-UV range is incomplete, and the values were therefore calculated by fitting the measured n dispersion in the visible range (400-800 nm) with an exponential equation. This is shown in Fig. 4 for the 180 W sample, where a, b, c and d are the fitting coefficients. The k and n values thus calculated do not show clear differences among the films, and are listed in Table 2. Interestingly, the precision requirement for the calculation of the k value for the Si line is much higher than for the O line, due to its fewer oscillations.

The thickness of the three PEALD SiO$_2$ films was calculated from the measured elemental emission line according to Eq. 1 and is reported in Table 3. The film thicknesses calculated from O and Si lines are in good agreement with each other. Nevertheless, there is approximately 12 % deviation between the calculated values and measured results from ellipsometry, which is most likely due to inaccuracies

during the fitting of k or/and n. Surprisingly, this is opposite to the finding of Dorka *et al.* [9], where the thickness of a PECVD SiO$_2$ layer was consistently lower by ellipsometry than the value calculated by GDOES data. The reason for this deviation is not known.

The thickness calculated from the Si emission line allows to evaluate the accuracy of the calculation procedure through the thickness corresponding to a single oscillation. In Eq. 1, the thickness can be expressed as $t_i = m \times k_i$, where m is calculated as 93 nm. This would represent the thickness of a SiO$_2$ thin layer corresponding to one full oscillation (*i.e.* $k = 1$), which is in good agreement with the deduction that one oscillation in the Si emission line represents about a 100 nm-thick SiO$_2$ layer [9]. Indeed, the accuracy of k is essential to determine the thickness of one-hundred-nanometer grade film and it plays a dominant role over the refractive index during the calculation.

4 Conclusion Rf-GDOES measurements of ~ 150 nm SiO$_2$ thin films deposited by PEALD on Si wafers were carried out to study the effect of the plasma power during film deposition. The technique provided the possibility to measure the elemental composition along the film depth with high-enough resolution. The intensity of C and N seems to decrease when the set plasma power increases enough (≥ 180 W).

In addition, GDOES was used to evaluate the density and thickness of the SiO$_2$ film. The use of the intensity oscillations in the emission profiles to calculate the thickness of a transparent layer resulted to be challenging due to the limited film thickness and the number of oscillations. Nevertheless, monitoring the sputtering rate allows to identify the film structure properties.

In summary, high-throughput rf-GDOES analyses for SiO$_2$ thin films deposited by PEALD, in which the required lateral resolution is much lower than the depth resolution, could be used on a systematic basis to study thin films properties and their dependence on deposition parameters.

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