Investigation of PEALD SiO_2 thin films by rf-GDOES

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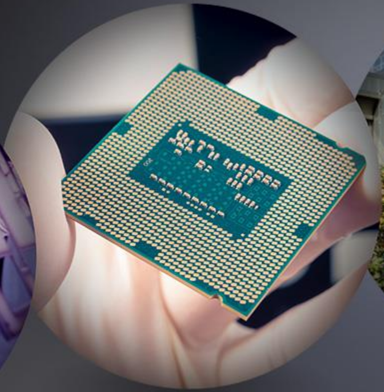

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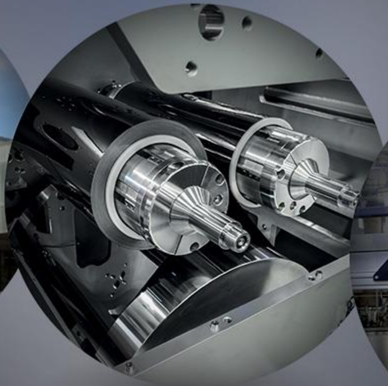

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Motivation - PEALD

- Thermal ALD (atomic layer deposition) is a thin-film growth method with many advantages:
  - conformality
  - ultra-thin film
  - repeatability
  - …
- PEALD (plasma enhanced ALD) provides further advantages:
  - It broadens applicable processing conditions (purge times, precursors, …)
  - It opens for a wider range of material properties (thermally sensitive substrates, …)
  - It shortens the deposition time

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Motivation – PEALD-SiO_2

- SiO_2 thin-films are a well-studied material.
- Nevertheless, properties of SiO_2 deposited by PEALD under varying process parameters are not widely understood:
  - Effect of plasma power?
  - Effect of plasma temperature?
  - Effect of plasma composition?
- Aim of our study:
  1. tackle the challenge of determining the **chemical composition** of PEALD-SiO_2 thin-layer (d < 200 nm) to understand the effect of **plasma power**
  2. use a fast technique for routine analysis

➔ rf-GDOES ?

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Introduction – rf-GDOES

- rf-GDOES (radio frequency glow discharge optical emission spectroscopy) is an effective analytical technique for thin film analysis
- Several advantages:
  - very good depth resolution (~ nm)
  - wide dynamic range (12 orders) ➔ detection limits (down to 1ppm)
  - multi-elemental analysis
  - fast analysis (few seconds-few minutes)
  - simple sample preparation
- Main limitation (not hindering analysis of ALD thin films):
  - mm-range lateral resolution

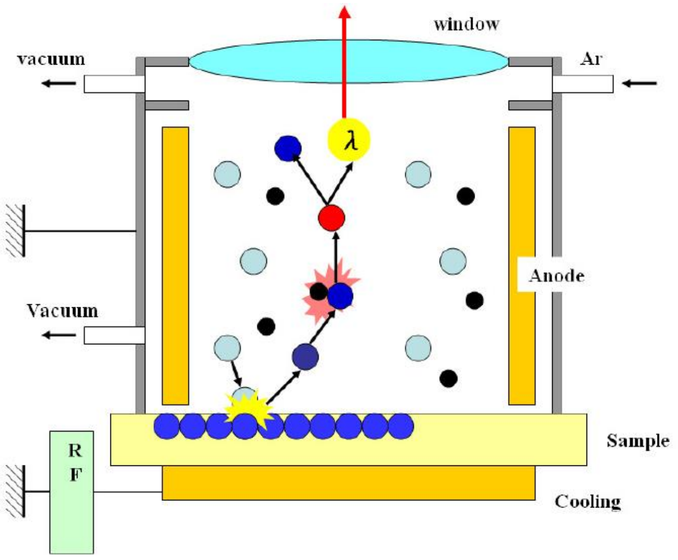
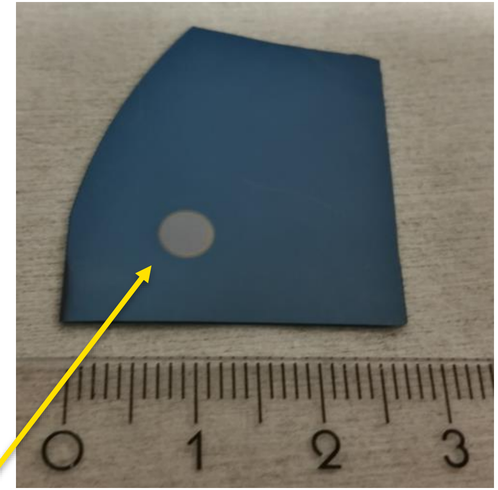


Photo and schematic diagram of the analytical GD source

Horiba, 2014

Materials

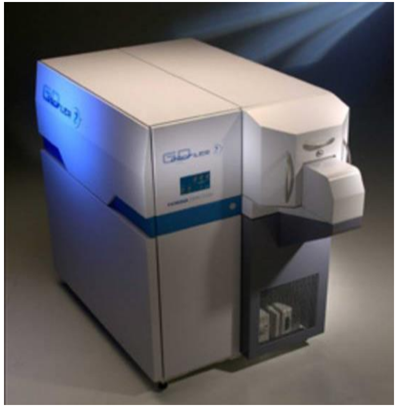


sputtered crater after GDOES measurement

- SiO_2 thin-films deposited on Czochralski Si substrates
- Deposition by O_2 – based PEALD and under varying plasma powers:
  - 50 W
  - 180 W
  - 300 W

Methods

- PEALD-SiO_2 deposition → Beneq TFS 200 reactor
- PEALD-SiO_2 compositional profiles (qualitative) → rf-GDOES Horiba Profiler2:
  - plasma power: 35 W
  - μs-pulsed discharge
  - pre-cleaning and flushing (surface cleaning)
  - total sputtering time < 20 s
- PEALD-SiO_2 thickness → ellipsometry and X-ray reflectivity
- PEALD-SiO_2 thickness → GDOES ?



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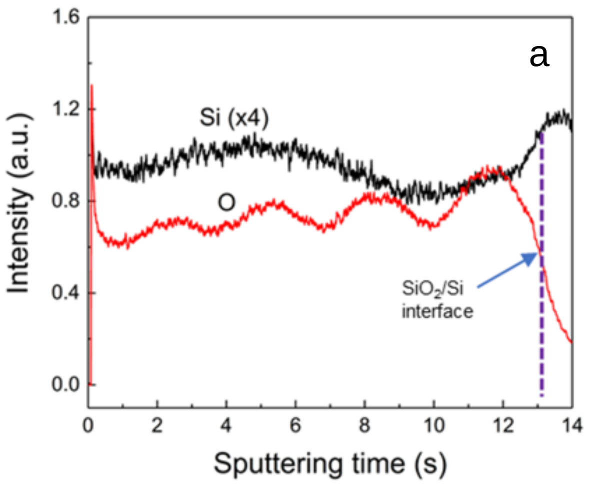
Qualitative elemental profiles

Example of elemental profiles for the PEALD-SiO_2 deposited at 180 W

matrix elements



➔ The matrix and main impurity elements were successfully analysed

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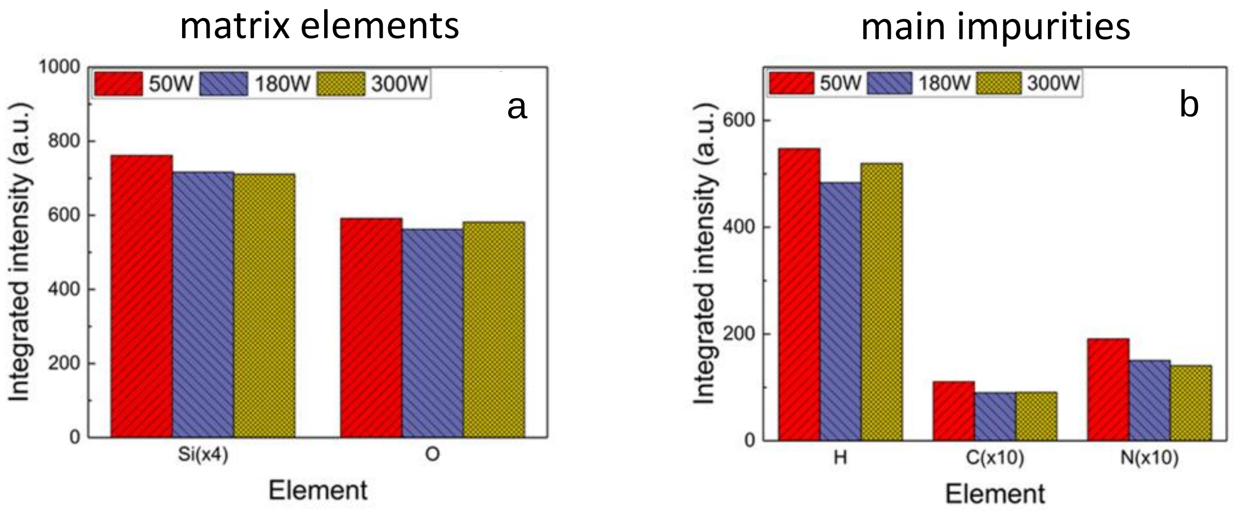
Chemical composition

- Intensities of elemental emission lines were integrated over the SiO_2 thin-film depth



- Intensity difference in Si, O and H is within the accuracy of the technique (±10%)
- Clear intensity difference in C and N ➔ lower content with increasing plasma power

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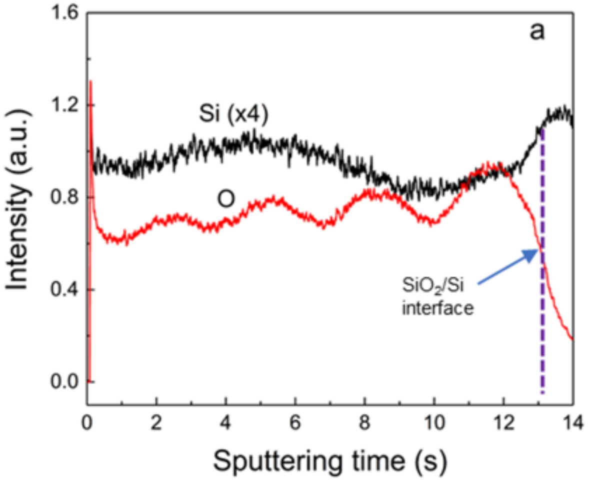
Structural properties

- Sputtering rate calculation:
  - same rate assumed for all films ➔ sputtering time divided by the thickness measured by ellipsometry ➔ calculation of the sputtering rate



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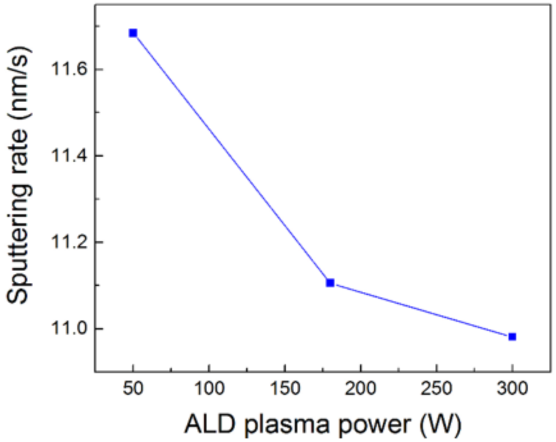
Structural properties

- Sputtering rate calculation:
  - same rate assumed for all films ➔ sputtering time divided by the thickness measured by ellipsometry ➔ calculation of the sputtering rate

- The sputtering rate decreases with increasing plasma power:

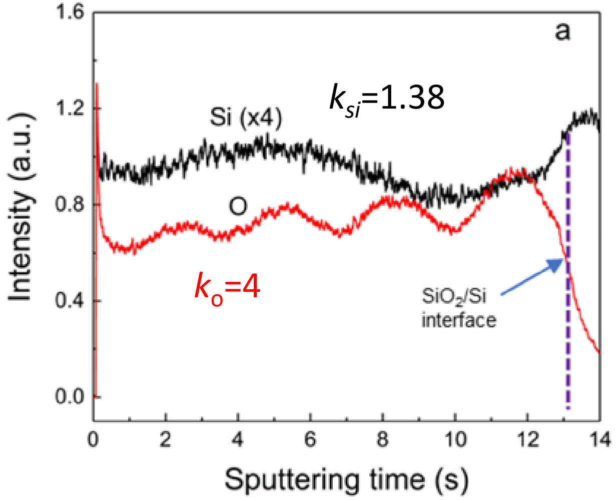


  - film thickness measured by ellipsometry is similar for all films (148nm @50W, 146nm @180W and 145nm @300W) ➔ reason for difference in sputtering time ?
  - it seems to be influenced by film density ⬄ measured density increase of ~ 5% with increasing plasma power (≥ 180W) (from XRR)

Calculation of the film thickness

- The thickness of a transparent thin film, *d* can be calculated as*:

$$d = \frac{k \times \lambda}{2 \times n}$$



- *k* is the number of oscillations of emission line *i* in the thin film
- *λ* is the wavelength of emission line *i*
- *n* is the refractive index of the thin film at wavelength *i*

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*Dorka, Kunze, Hoffmann, JAAS 2000, **15**, 873-876

Calculation of the film thickness

- Comparison of thickness calculated from GDOES *vs* from reference techniques (ellipsometry and XRR):

Method	PE-ALD SiO_2 thickness	PE-ALD plasma power		
		50W	180W	300W
GDOES	d_O (nm)	129	128	128
	d_{Si} (nm)	129	128	127
Ellipsometry	d from ellipsometry (nm)	148	146	145
XRR	d from XRR (nm)	148	147	147

→ Note that $\frac{\lambda}{2\times n}$ = 93 nm (corresponding to the thickness for *k* =1) ⇔ good agreement with 100 nm value as suggested by Dorka *et al.**

→ Thus, for thin films (*d* < 200 nm), the relevance of the accuracy of *k* is dominant over the refractive index for the calculation of *d*.

*Dorka, Kunze, Hoffmann, JAAS 2000, **15**, 873-876

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Summary

- **GDOES** analysis provided important information on the **chemical and structural properties** of **PEALD SiO_2 thin films**, with good depth resolution and fast analysis.

- Detection limits are sufficient for the analytical purposes.

- GDOES analysis of thin (< 200 nm), transparent layers is challenging.

- The calculation of the thickness is severely affected by the number of oscillations *k* in the elemental lines, which cannot be rounded to the closest integer for small *k* values.

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Thank you for your attention!

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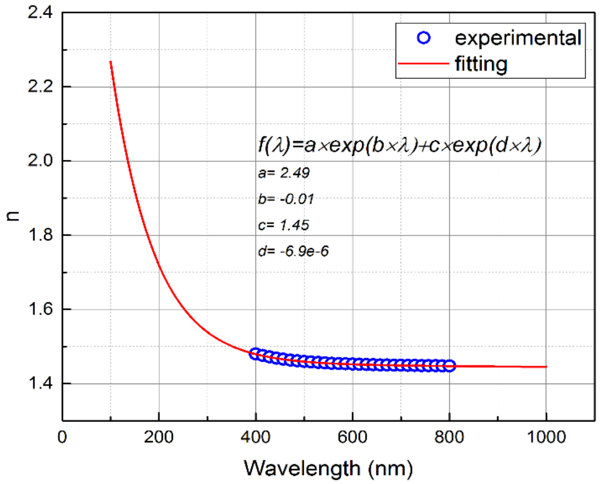
Calculation of the film thickness

- The thickness of a transparent thin film, d can be calculated as*:

$$d = \frac{k \times \lambda}{2 \times n}$$

  – *n* is the refractive index of the thin film at wavelength *i*

- Example of the simulated refractive index, n of the sample deposited at 180 W.
- The fitting is done on the measured values in the visible range.



*Dorka, Kunze, Hoffmann, JAAS 2000, **15**, 873-876

Calculation of the film thickness

- Influence of the number of oscillations within the film thickness:

SiO_2	50W	180W	300W
k@130nm (O line)	4	4	4
n@130nm (O line)	2.018	2.035	2.030
k@288nm (Si line)	1.38	1.38	1.37
n@288nm (Si line)	1.545	1.552	1.556

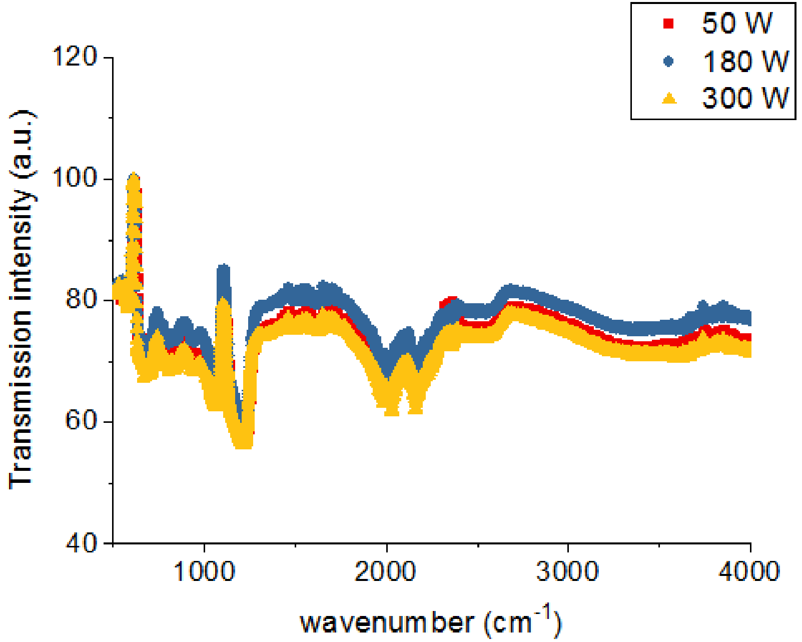
Note that *n* is assumed to be constant throughouot the whole film thickness

→ Thus, for thin films (*d* < 200 nm), the relevance of the accuracy of *k* is dominant over that of the refractive index for the calculation of *d*.

*Dorka, Kunze, Hoffmann, JAAS 2000, **15**, 873-876

Infrared spectrometry

- Qualitative analysis
- FTIR does not show clear differences among the thin films
- Transmission is also influenced by the Si substrate ➔ limitation for possibility of evaluation of spectra



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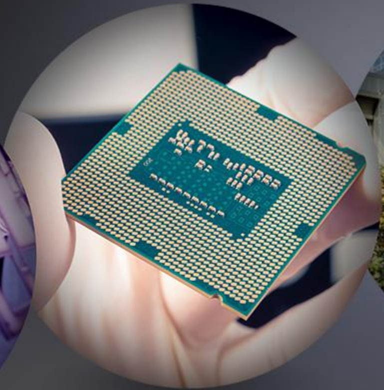

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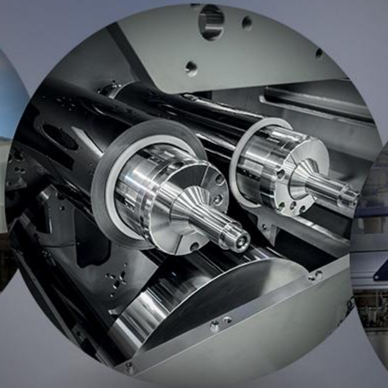

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