Organic framework engineering for VOC sensing in mesoporous SiO_2 films

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We have studied dense and porous SiO_2 films deposited by the sol-gel and evaporation induced self-assembly methods using different organic templates – Pluronic PE6400 and PE9400 (BASF). By using UV-Vis spectroscopy the films' refractive indices and thicknesses were calculated from their spectra via non-linear curve fitting method. Porosity of the films and acetone vapor saturation after exposure are quantified by implementation of Bruggeman effective medium approximation. The change in refractive indices because of the acetone exposure process gives us an opportunity for possible application of the films as an active medium for chemo-optical detection.

Film deposition

Sol – gel method

HCl – 0,2 ml
H2O – 0,75 ml
EtOH – 4,4 ml
TEOS – 6 ml
(100ml)
+
Ethanol (600ml)

200 ml

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H2O – 0,75 ml
EtOH – 4,4 ml
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(100ml)
+
Ethanol (600ml)

5:1 volume ratio of dissolved in ethanol organic template

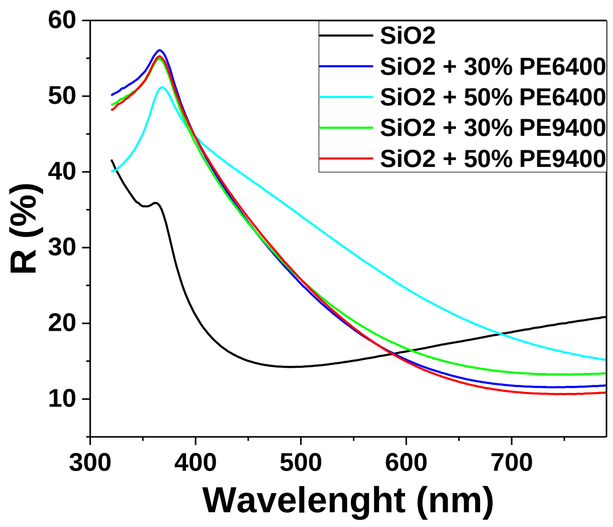
200 ml

Spin coating – 4000 min^{-1} for 60 s
Annealing – from 20°C to 320°C, 5°C per min

→ Dense film

→ Porous film

Optical properties



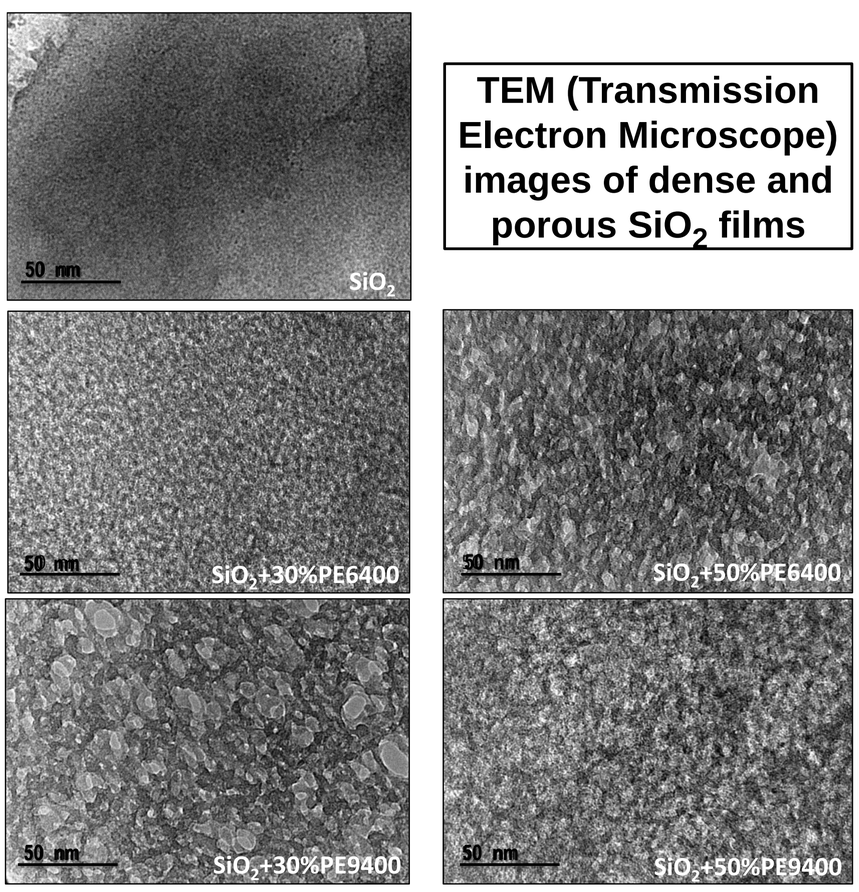
We used UV-Vis spectrometer to measure the reflection spectra of the films

The SiO_2 thin films were deposited on silicon substrates

- ❑ The addition of a polymer makes the films thicker
- ❑ The thicknesses and refractive indices of the films are calculated numerically from the reflection spectra using non-linear curve fitting approximation

Film	Thickness (nm)	Refractive index (600 nm)
SiO_2	82	1,43
SiO_2+30% PE6400	132	1,35
SiO_2+50% PE6400	170	1,26
SiO_2+30% PE9400	137	1,3
SiO_2+50% PE9400	134	1,37

Surface morphology and pore formation



TEM (Transmission Electron Microscope) images of dense and porous SiO_2 films

The Pluronic PE types are block copolymers in which the central polypropylene glycol group is flanked by two polyethylene glycol groups.

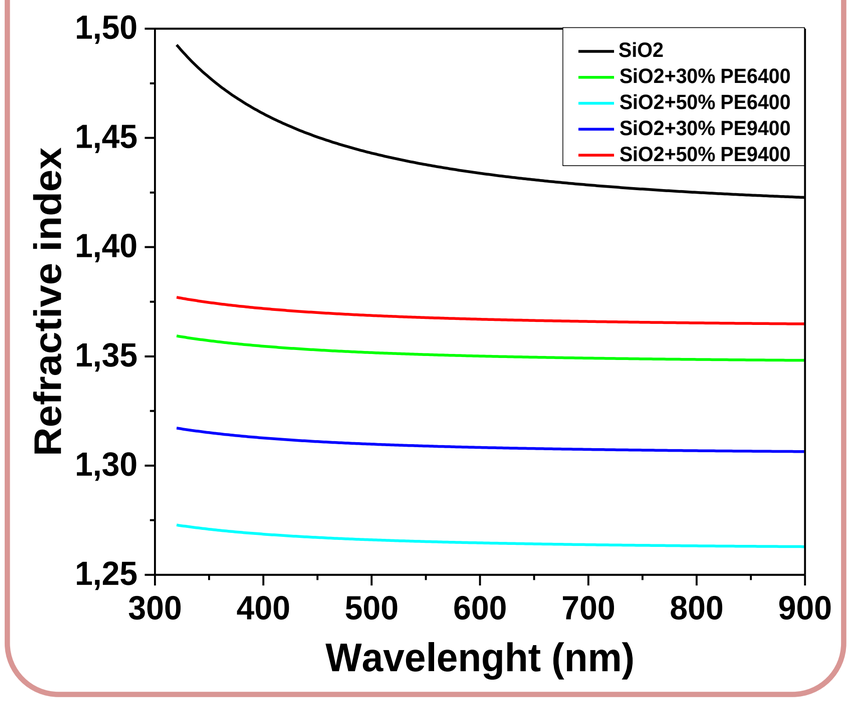
	PE 6400	PE 9400
Molar mass of PPG (g/mol)	1750	2750
PEG in molecule (%)	40	40

PPG – Polypropylene glycol
PEG – Polyethylene glycol

- ❖ *The porous films are prepared by evaporation-induced self-assembly method where the copolymers act as pore templates*
- ❖ *The template is eliminated by annealing thus leaving only the porous films*

The images show that the increase of PE6400 concentration makes the pores bigger whereas for PE9400 it is the opposite case

Dispersion of refractive index



Porosity evaluation

In order to calculate the free volume fraction of the film Bruggeman effective medium approximation has been used:

$$f_d \frac{\varepsilon_d - \varepsilon_e}{\varepsilon_d + 2\varepsilon_e} + f_{air} \frac{\varepsilon_{air} - \varepsilon_e}{\varepsilon_{air} + 2\varepsilon_e} = 0$$

$$f_d + f_{air} = 1$$

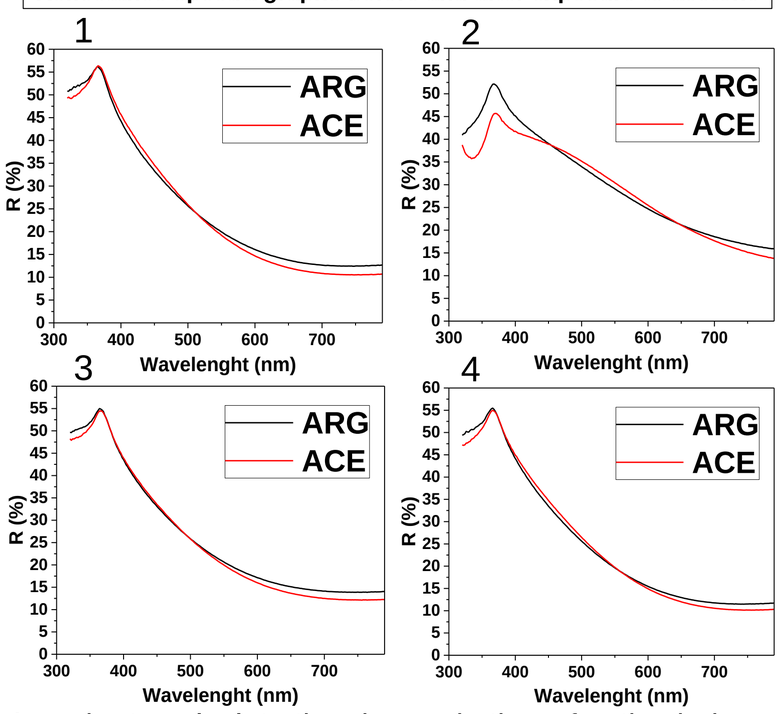
ε_d, ε_{air}, ε_e - dielectric constants of dense SiO_2, air, and effective medium,
f_d, f_{air} – volume fractions of dense SiO_2 and air

So using Pluronic PE types as pore templates we have successfully created free volume fractions in the films thus making them fitting for further testing

Porous film	Porosity (%)
SiO_2+30%PE6400	20
SiO_2+50%PE6400	39
SiO_2+30%PE9400	29
SiO_2+50%PE9400	16

Acetone exposure

Reflectance spectra graphs before and after exposure to acetone



Porous film	Change in refractive index
[1]SiO_2+30% PE6400	0,04
[2]SiO_2+50% PE6400	0,07
[3]SiO_2+30% PE9400	0,05
[4]SiO_2+50% PE9400	0,06

The SiO_2 porous films are put in a cell which is then filled with argon to clear the air inside and with acetone vapors afterwards

In order to calculate the change in the refractive index we use the following formulas:

$$\Delta R_{Ac} = \frac{\partial R_{Ac}}{\partial n} \Delta n$$

$$\frac{\partial R_{Ac}}{\partial n} = \frac{|R_1 - R_2|}{2\delta}$$

Where ***∂Rac/∂n*** is the partial derivative of ***Rac*** with respect to n and R_1 and R_2 are reflectance values calculated for two different values of refractive index ($n_a+\delta$) and ($n_a-\delta$), where δ is a very small deviation from n_a (n_a is the refractive index after saturation)

Conclusions

The increase in polymer concentration leads to:

- **Bigger change in the refractive index of the mesoporous films after the acetone exposure procedure in both the cases of PE6400 and PE9400 (the greatest change was achieved for 50%PE6400 - 0,07)**
- **More free volume space in the mesoporous films in the case of PE6400 and less in the case of PE9400**

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