Acetone sensing with optical readout using SiO_2 thin films

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The reflectance spectra of thin silica films depend on the thickness and refractive index. As a result, the optical characterization of the films becomes the most important basis for studying their sensing applications with optical read-out.

Thin silica films are prepared by spin-coating deposition and subsequent high temperature annealing. Dense samples of thin SiO_2 films are deposited on silicon substrates without organic template. Soft-template method is employed to generate free volume within the films and to obtain porous samples.

Reflectance spectra are measured prior to and after exposure to acetone vapors and by implementation of non-linear curve fitting method refractive index and thickness of the films are calculated. Surface morphology and structure of the porous films depend on the characteristics of the triblock copolymer used as template and are studied by transmission electron microscopy. Using Bruggeman effective medium approximation the overall porosity of the films is quantified.

Film preparation

- Sol – gel method: Stöber process

0.2 mL 36% HCl
0.75 mL H_2O

4.4 + 68.1 mL EtOH
6 mL TEOS

5:1 (volume ratio) =
= Si-sol : dissolved
in ethanol Pluronic PE

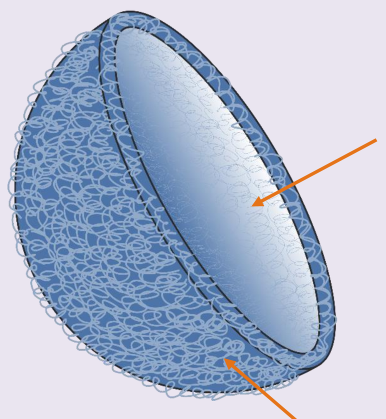
Spin coating - 4000 min^{-1}, 60 s
Annealing (from 20 ^{0}C to 320 ^{0}C, 5 ^{0}C/min)

Dense SiO_2 film

Porous SiO_2 film

Surfactants used:
Pluronic PE 6200, Pluronic PE 6800

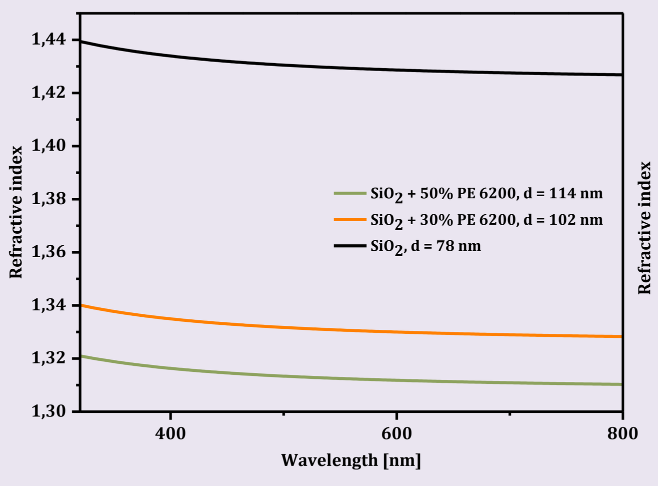
Micelles formation

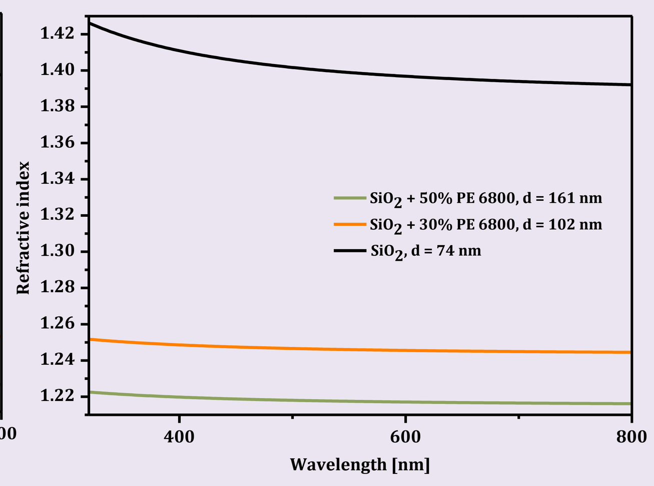


The addition of surfactants to the reaction mixture leads to changes in morphology of the SiO_2 particles. The surfactant forms micelles and the silica network grows around the hydrophilic surface, producing particles with surfactant- and solvent-filled channels. The thermal treatment leads to removal of the surfactant and solvent molecules (by combustion and evaporation). Throughout the structure are present mesopore voids.

	PE 6200	PE 6800
Molar mass of PPG (g/mol)	1750	1750
PEG in molecule (%)	20	80

Optical characterization



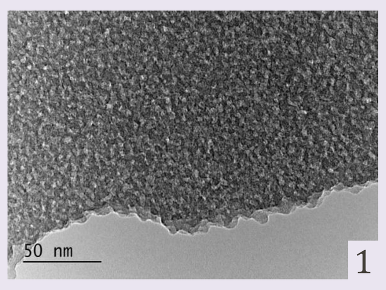


From the reflection spectra of the films, their thickness (d) and refractive index (n) dispersion have been obtained. The refractive index dispersion have been calculated in terms of the Wemple-diDomenico single oscillator model.

The values of n at wavelength of 600 nm decrease from 1.43 for the dense film to 1.37 for porous films with PE 6200 and from 1.40 to 1.25 and 1.22 for porous films with PE 6800 concentration of 30% and 50%, respectively.

Surface morphology

1) Porous SiO_2(30% PE 6200)
2) Porous SiO_2(50% PE 6200)
3) Porous SiO_2 (30% PE 6800)
4) Porous SiO_2 (50% PE 6800)
5) Dense SiO_2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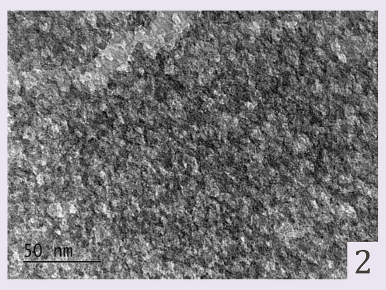
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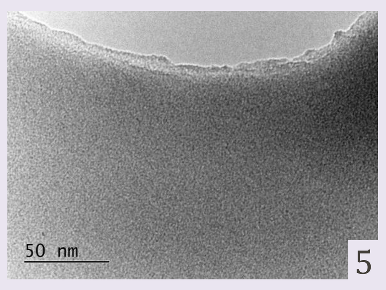
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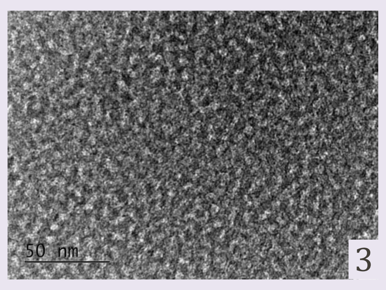
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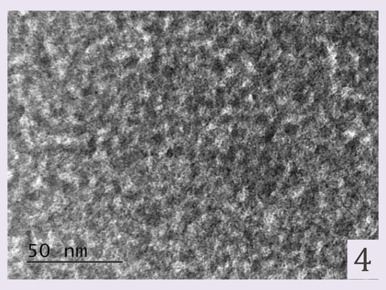
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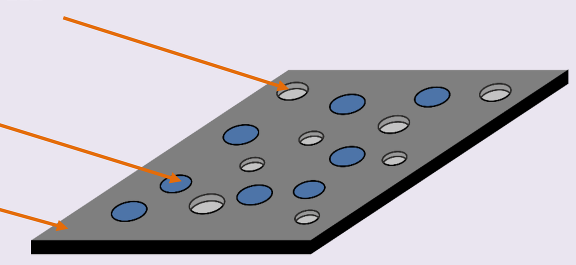
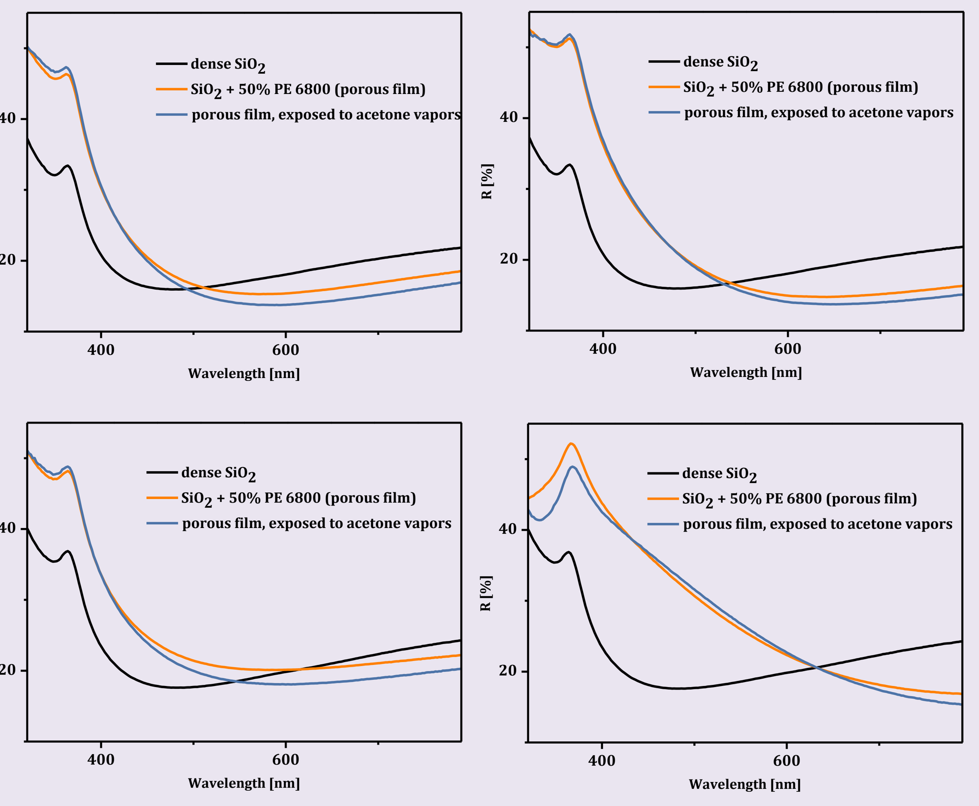
The comparison of morphology shows that the organic template leads to the formation of pores arranged nonperiodically.

VOC sensing



The exposure of the porous films to acetone results in vapor condensation in the pores and change of its reflectance spectrum.



Porosity evaluation

The replacement of the air in the pores with acetone with higher refractive index leads to increase of the effective refractive index of the films.

- Bruggeman effective medium approximation

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

$$f_d + f_{air} = 1 \qquad \varepsilon_i = n_i^2$$

$\varepsilon_d, \varepsilon_{air}, \varepsilon_e$ - dielectric constants of dense SiO_2, air, and effective medium
f_d, f_{air} – volume fractions of dense SiO_2, and air

	max ΔR = $\lvert R_{Acetone} - R_{ar}\rvert$	Δn	f_{air}
SiO_2+ 30% PE 6200	2.11% (at λ=676 nm)	0.04	10%
SiO_2+50% PE 6200	1.72% (at λ=764 nm)	0.03	9%
SiO_2+ 30% PE 6800	2.36% (at λ=636 nm)	0.04	10%
SiO_2+50% PE 6800	1.07% (at λ=506 nm)	0.08	22%

Conclusion

- The introducing of porosity in the deposited films and their consequent thickness growth is associated with reduction of the refractive index. In such a way a free volume in the films is generated reaching 22% that leads to change of the effective refractive index of 0.08 when exposed to acetone vapors.
- Higher polymer concentration enhances the thickness and more PEG in polymer molecule favors the increase of the thickness difference between dense and porous film as compared to the case when PPG is prevailing.
- Varying the surfactant concentration allows control over the diameter and volume of pores and the surface morphology of the films. Using PE 6800 as surfactant leads to formation of better developed pores.

Acknowledgements

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