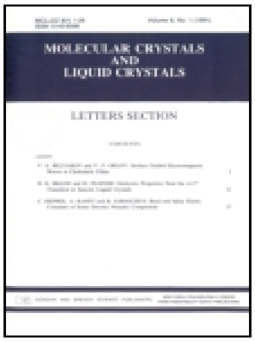

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Mesoporous materials from SiO_2 and $NiTiO_3$

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ABSTRACT

In this work, we synthesized and characterized mesoporous thin films of SiO_2 and $NiTiO_3$ structured by a surfactant called Brij58. These films were fabricated by the method of dip coating and the best conditions for well-structured thin films were investigated as a function of surfactant concentration and different types of substrates. These films have been characterized by X-ray reflectivity which was calculated using the matrix formalism. We demonstrated that the silicon substrate had a great effect on the structure and porosity of the fabricated films for both SiO_2 and $NiTiO_3$. Furthermore, we found that mesoporosity has been increased as a function of the surfactant concentration in the solution. This experimental procedure allows also to produce $NiTiO_3$ powders which have been characterized by X-ray diffraction. The XRD coupled to the crystallographic software "Maud"shows that the samples are constituted by 98, 2% $NiTiO_3$ powders.

KEYWORDS

Mesoporous thin films; dip coating; brij58; X-ray reflectivity

1. Introduction

In the last decades, porous materials become the subject of several studies. According to IUPAC (International Union of Pure and Applied Chemistry) [1] they are defined by the pore size and are classified into three categories:

- The microporous materials with pore diameters less than 2 nm ($dp<2$ nm),
- The macroporous materials having sizes of pores greater than 50 nm ($dp> 50$ nm) [2],
- Finally mesoporous materials with pore diameters between 2 and 50 nm (2 nm $<dp<50$ nm) [3].

Mesoporous materials are obtained by mixing an organic surfactant with the precursor of an oxide such as silica involving the sol-gel chemistry. The most cited applications are technical applications such as catalysis [4], filtering [5], nanofluidic [6], chromatography [7], gas storage and encapsulation materials [8], Sensors [9] and the controlled delivery medicines [10]. Subsequently, several groups tried to elaborate these materials in the form of thin films. In this work, we investigated the elaboration of mesoporous materials structured by a nonionic surfactant known by the acronym of Brij58 using sol-gel technique.

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2. Experimental procedure

Mesoporous films are fabricated by the method of self-assembly induced by solvent evaporate ion. This procedure, known as the EISA (Evaporation-Induced Self-Assembly) [11] is very well known for the synthesis of mesoporous thin films by sol-gel.

First, we prepared the initial SiO_2 solution for different concentrations of Brij 58; a given mass of Brij58 is dissolved in 36.79 g of pure Ethanol, in such manner to obtain a perfectly homogeneous solution by agitation during ten minutes. To this solution, we add 0.8g of pure water, 0.21g of hydrochloric acid and 2.5g of tetra ethyl ortho silicate (TEOS) and the resulting mixture was aged for a time under magnetic stirring at room temperature.

To obtain surfactant structured $NiTiO_3$ films; we prepared solutions with a given mass of Brij 58 dissolved in 31.4 ml of pure ethanol and 1ml of nitric acid (HNO_3). After that the solution was introduced during ten minutes in an ultrasonic bath to obtain a perfectly homogeneous mixture. We prepared second solution containing 1, 2g of the Nickel acetate tetrahydrate (NA), 0, 66ml of nitric acid (HNO_3) and 1, 46ml of titanium isopropoxide (TIP), dissolved in 2, 28 ml of pure ethanol. Finally, we mixed the two solutions and we aged for a given time under magnetic stirring at room temperature.

The mass of the Brij 58 is calculated from a percentage of the surfactant mass ($\varphi[\%]$) following the equation:

$$\varphi(\%) = \frac{m_{Brij}}{m_{Brij} + m_{SiO_2}} \times 100 \tag{1}$$

$$m_{Brij} = \frac{m_{SiO_2}}{\left(\frac{1}{\varphi} - 1\right)} \tag{2}$$

Before the deposition of the films we cleaned substrates; this step is very important to avoid any organic contamination. For this, the wafers are cleaned with acetone in an ultrasonic bath for 5 minutes to remove the organic waste and then the substrates are washed with ethanol for 5 minutes in an ultrasonic bath to remove the acetone and dried with compressed air.

Then the films were deposited on the substrates by the dip-coating technique; it consists in immersing the substrate in the solution for a while and then removing the substrate from the solution at a constant speed to obtain a film of uniform thickness [12], during removal, the solution will flow along the substrate. At the end of flow, the substrate is covered with a uniform porous film. The extraction speed affects the film thickness, which increases with the drawing speed, but it also depends on the concentration of solute and solvent. The relative humidity (RH) in the dip-coater plays a crucial role in the structuring of thin films. The humidity and temperature inside the dip coater were controlled automatically using a controller managed by (ROTRONIC HW3 Hygro Win) software.

2.2. *Characterization techniques*

Analyses were made using a diffractometer 'Empyrean Panalytical'. The reflectivity spectra were recorded with a copper anticathode ($I = 30$ mA and $V = 40$ KV) using copper $K\alpha$ radiation of wavelength $\lambda = 1.54056$ Å with a detector 'Pixel 3D'. Scanning was done in three stages:

- Ref1: $0.1 < 2\Theta < 1.24$;with a step of 0.01 and a time of 1 s.
- Ref2: $1.24 < 2\Theta < 3.04$;with a step of 0.01 and a time of 5s.
- Ref3: $3.04 < 2\Theta < 10$;with a step of 0.04 and a time of 10s.

The calculation of X-ray reflectivity curves is done via the matrix technique, written by William Vignaud and Alain Gibaud [13, 14], on Matlab. This program requires some input parameters and characteristics of the deposited material. A simple qualitative analysis of the experimental curves allows to access to the number of periodic layers present in each sample, their thicknesses, and their average electron density.

XRD analysis of the crystalline phase existing in the powders was made using a diffractometer X'pert. X-Ray diffraction spectra were recorded with copper anticathode (I = 30m A and V = 40 KV) using the K_α copper radiation wavelength $\lambda = 1.54056$ Å. The diffractometer is coupled to a computer which allows the installation control, acquisition, storage and processing of data. Structural information is obtained from a powder pattern collected in the angular range 2θ: 20–100° with an angular pitch of 0.04 and a counting time of 20 seconds per step.

3. Results and discussion

After synthesizing the mesoporous films of SiO_2 deposited on glass and silicon substrates, all sample were annealing at 80°C for 48 hours in an oven allowed the condensation of the gel. The sample was washed with ethanol and dried in an oven at 80°C for 1h30min, allowing to remove completely the surfactant and obtaining pure mesoporous silica film.

We can see from reflectivity curves that the increase in concentration of Brij58 is accompanied by an increase in the number of Kiessig fringes. This phenomenon can be explained by the fact that an increase of the concentration of Brij58 produces an increase of the solution viscosity and consequently increases the film thickness. This phenomenon is well known in the dip-coating method the thickness of the elaborated film is directly related to the solution viscosity. Moreover, as we can see in Figure (1) and Figure (2), the reflectivity curves show that the films are well structured for concentrations 35%, 43%, 53% and 62%. The absence of the second Bragg peak for the corresponding curves at the concentrations 35% and 43% can be explained by the fact that the silica wall is as thick as the stratum containing the surfactant. Another explanation is possible considering the roughness. Indeed, if the roughness is very important the intensity of the second peak of Bragg be overlooked.

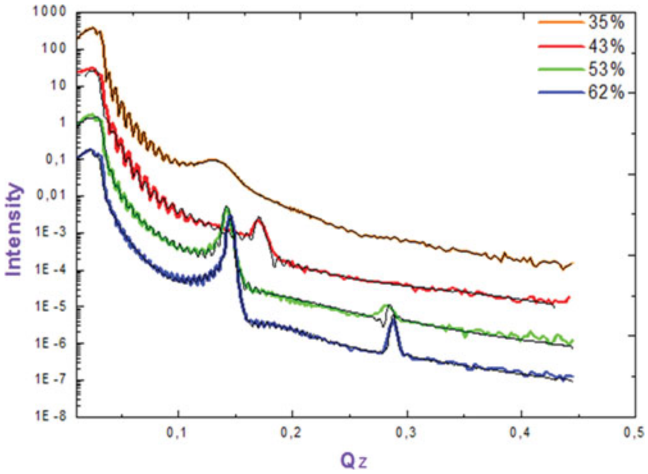

Figure 1.

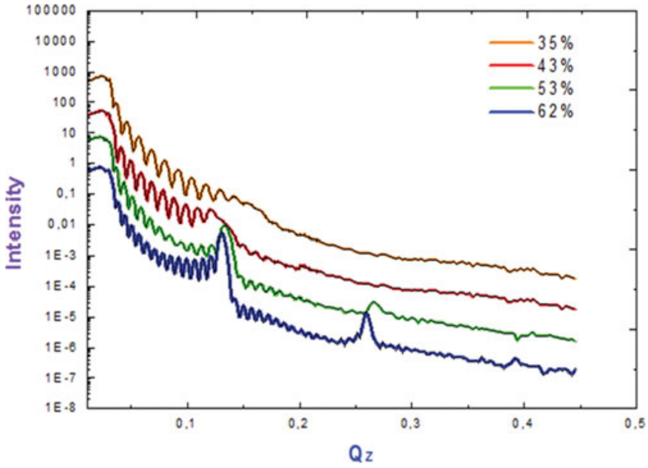

Figure 2.

The two figures (3) and (4) represent the reflectivity curves of the films deposited on washed glass and silicon substrates for different concentrations of Brij58, for each concentration, we can see a shift of the Bragg peaks to the large values after the extraction of the surfactant.

The mesoporous films of silica concentration 53% Brij 58 were used to study the possible influence of the substrate on which we make filing our films. The study focused on two types of substrates: the glass and silicon.

In the case of glass substrate: the reflectivity curves corresponding to the unwashed film and at the film washed with ethanol, obtained at a concentration of 53%, are analyzed using the matrix technique.

The extraction of the surfactant produces a shift of the critical Angles qc 0.025–0.022Å^{-1} as shown in Figure (5), this shift produces a decrease in the electron density reflects the existence of pores in the film. Note also that both the Bragg peaks of the mesoporous thin film reflectivity curve located at positions 0.13 Å^{-1} and 0.27 Å^{-1} are moving to the great values of qc after washing with pure ethanol positions 0.16 Å^{-1} and 0.31 Å^{-1}. This displacement of the

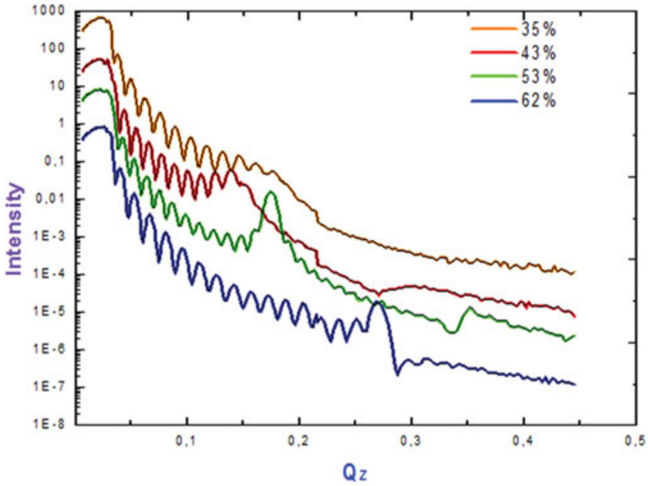

Figure 3.

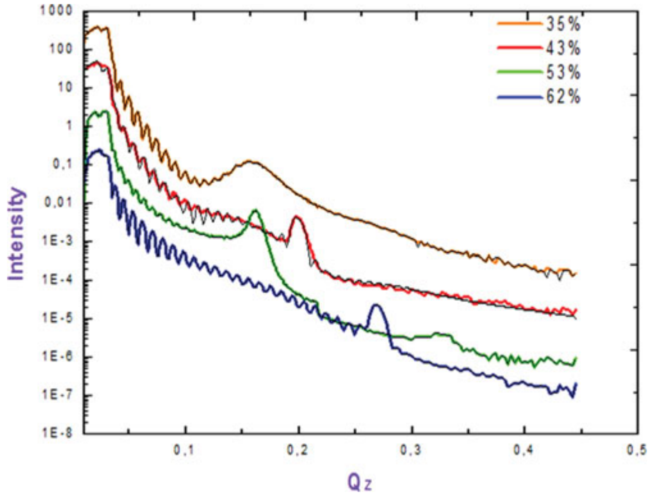

Figure 4.

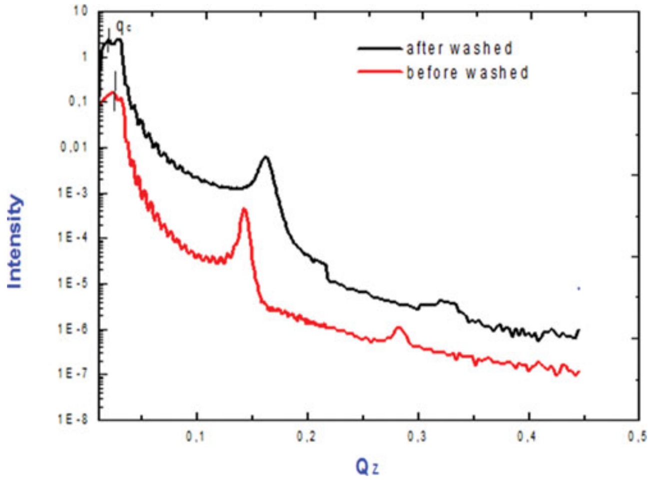

Figure 5.

Bragg peaks, after extraction of the surfactant results in the decrease of the period T of the pattern which passed from 4.9 nm to 4.2 nm.

With silicon substrate : the results of the reflectivity curves before and after rinsing the samples are presented in Figure (5) and the structural parameters extracted from these curves are dressed in Table (1). These parameters are in perfect agreement with the values estimated by the model based on matrix formalism.

Table 1. Experimental parameters of unwashed and washed SiO_2 mesoporous Films deposited on the glass substrate for 53% concentration of Brij58 surfactant after refinement.

	qc ($Å^{-1}$)	σ (Å)	e (Å)
Substrate	0.0318/0.0318	05.40/08.17	—
Film-substrate interface	0.028/0.0230	06.30/00.20	20.40/16.84
Layer 1	0.0230/0.0280	09.10/09.75	32.10/19.62
Layer 2	0.0270/0.0210	10.10/11.71	12.70/22.60
Film-air interface	0.0160/0.0280	00.90/07.05	24.20/08.30

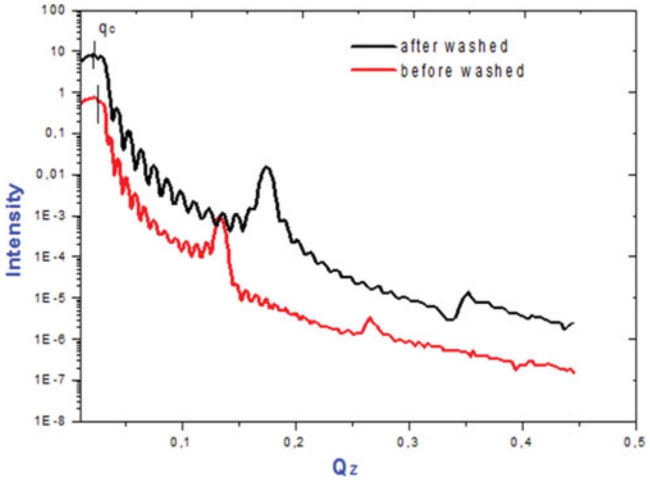

Figure 6.

The analysis of the reflectivity curves allowed to calculate the average electron density of SiO2 film and was estimated to be equal to 0.44 e-/Å^3 and mesoporosity of a film is estimated of about 21%.

The reflectivity curves of films fabricated with 53% of the surfactant are presented in Figure (6), in both cases where film washed or not. The same shift of the critical wave vector of 0.025 to 0.02 Å^{-1} after rinsing the film ethanol. This shift reflects the decrease in the electron density of the film after extraction of the surfactant.

The electron density average of the washed and unwashed film based on data given in Table (2) is the same result to that found for the film obtained with the glass, as a substrate and mesoporosity of a such film is estimated at 39%.

We note that the mesoporosity of the film obtained with the silicon substrate is greater than that obtained with the glass substrate. This suggests that the structural properties of the obtained films are affected by the surfactant concentration and also by the type of substrate.

Table 2. Experimental parameters of unwashed and washed SiO_2 mesoporous films deposited on the silicon substrate for 53% concentration of Brij58 surfactant after refinement.

	qc (Å^{-1})	σ (Å)	e (Å)
Substrate	0.0318/0.0318	3.4/5.1	—
Film-substrate interface	0.0290/0.0274	5.4/0.5	9.8/15.0
Layer 1	0.0225/0.0304	10.5/13.0	33.0/24.0
Layer 2	0.0282/0.0232	12.0/9.0	13.4/23.6
Film-air interface	0.0181/0.0226	2.1/6.6	24.0/10.1

Table 3. Experimental parameters of $NiTiO_3$ mesoporous Films deposited on the silicon substrate after refinement for 50% concentration.

	qc (Å^{-1})	σ (Å)	e (Å)
Substrate	0.0318	05.90	—
Film-substrate interface	0.0309	01.120	31.96
Layer 1	0.0260	12.33	33.43
Layer 2	0.0296	13.10	16.64
Film-air interface	0.0167	17.90	20.07

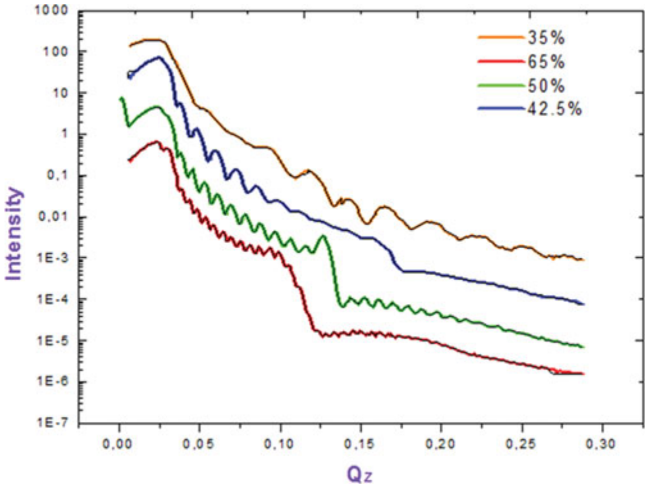

Figure 7.

After synthesis of the $NiTiO_3$ mesoporous films, a heat treatment of the sample is carried out at 80°C for 2 Hours in an oven allowed the condensation of the gel.

The reflectivity curves show that well-structured film for the 50% concentration, beyond this value of concentration, the films are not well structured as we can see in the Figure (7).

3.1. X-ray diffraction (XRD)

$NiTiO_3$ powder is prepared from solution containing 65% Brij58. The solution was dried on a heat plate at 70°C for several hours. The resulting gel was then placed in a furnace to be dried at 400°C for 2 hours. Finally, the obtained powder was annealed at 600°C for 2 hours.

XRD results are shown in Figure (8). The phases identification were studied by crystallographic software “Maud” created by L. Lutterotti [15], this program allows to refine the

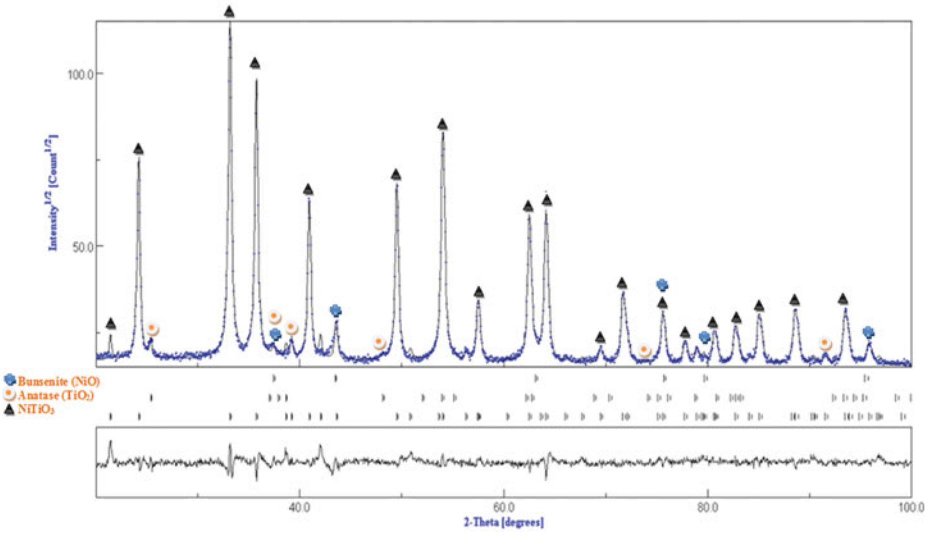

Figure 8.

diffraction patterns by adjusting the lattice parameters and other parameters such as the size of the crystallites, deformation of the lattice and the preferential orientation.

Note that the profiles shown above are characterized by three phases in the R-3 space group, the X-ray diffraction shows the existence of a phase: $NiTiO_3$ of percentage of 98.2% and two phases in the form of Anatase (TiO_2) and bunsenite (NiO) impurities of percentage of 1.23 and 0.6%. The $NiTiO_3$ lattice parameters after the refinement are: $a = b = 5.0350$Å, $c = 13.8159$Å, $\alpha = \beta = 90°$, $\gamma = 120$ and the volume $V = |a. (b \wedge c)|$ is considered to 303.32 $Å^3$.

4. Conclusion

We succeeded to synthesize and to characterize thin films of mesoporous structured by a surfactant called Brij58. These films were formed by dip-coating, the conditions for well-structured thin films were studied as a function of surfactant concentration and the choice of substrates on which we make the deposit of our films. Then, we characterized these films by X-ray reflectivity and using data obtained by calculating matrix formalism, we note that the films are well structured with the following mass concentrations: 53% and 62% on silicon substrate. Accordingly, we notice while mesoporosity has been increased as a function of the amount of surfactant in solution.

Furthermore, we have also synthesized $NiTiO_3$ powders which were characterized by X-ray diffraction. The results of XRD were investigated using crystallographic software "Maud." The diffractogram shows the existence of 98.2% as a percentage of $NiTiO_3$ which was described in the hexagonal trigonal system of R-3 space group.

Acknowledgments

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References

[1] Burwell, R. L. J. R. (1972). IUPAC: Manual of symbols and terminology, appendix 2, Pont 1. Colloid and surface Chemistry. *Pure Appl. Chem.*, *31*, 578.
[2] Sing, K. S. W., Evertt, D. H., Hual, R. A. W., Mocsou, L., Pierotti, R. A., Rouquerol, J., & Siemienievska, T. (1985). IUPAC. *Pure Appl. Chem.*, *57*, 603.
[3] McCusker, L. B., Liebau, F., & Engelhardat, G. (2001). *Pure and Applied Chemistry*, *73*, 381–394.
[4] Taguchi, A., & Schuth, F. (2005). *Microporous and Mesoporous Materials*, *77*:1–45.
[5] Park, D. H., Nishiyama, N., Egashira, Y., & Ueyama, K. (2001). *Ind. Eng. Chem. Res*, *40*, 6105.
[6] Fan, H., Lu, Y., Stump, A., Reed, S. T., Baer, T., Schunk, R., Perez-Luna, V., Lopez, G. P., & Brinker, C. J. (2000). *Nature*, *405*, 56–60.
[7] Unger, K. K., Kumar, D., Grun, M., Buchel, G., Ludtke, S., Adam, T., Schumacher, K., & Renker, S. (2000). *Journal of Chromatography A*, *892*, 47–55.
[8] Domansky, K., Liu, J., Engelhard, M. H., Wang, L. Q., & Baskaran, S. (2001). *J. Mater. Res*, *16*, 2816.
[9] Innocenzi, P., Martucci, A., Guglielmi, M., Bearzotti, A., & Traversa, E. (2001). *Sensors and Actuators*, *B57*, 2049.
[10] Huang, X., Young, N. P., & Townley, H. E. (2014). Characterization and Comparison of Mesoporous Silica Particles for Optimized Drug Delivery. DOI: 10.5772/58290.
[11] Brinker, C. J., Lu, Y., Sellinger, A., & Fan, H. (1999). *Adv. Mater.*, *11*, 579.
[12] Brinker, C. J., & Hurd, A. J. (1994). *J. Phys. III France*, *4*, 1231.

[13] Dourdain, S., Bardeau, J. F., Colas, M., Smarsly, B., Mehdi, A., Ocko, B. M., & Gibaud, A. (2005). *Appl. Phys. Letters*, *86*, 113108, 84.
[14] Gibaud, A, Dourdain, S., & Vignaud, G. (2006). *Appl. Surface Science*, *253*, 3–11, 84.
[15] Dourdain, S. (2006). *thesis : caractérisation structurale, poreuse et mécanique de films minces de silice mésoporeux. Influence de la fonctionnalisation*, University du Maine.