Applied Surface Science 256S (2009) S18–S21

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Mesoporous silica layers with controllable porosity and pore size

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ARTICLE INFO

Article history:
Available online 18 April 2009

PACS:
42.79.Wc
68.08.Bc

Keywords:
Thin film
Porosity
Structure and morphology
Optical coatings
Refractive index

ABSTRACT

Silica layers with controllable porosity and pore size were prepared via a templating approach. The structure of these mesoporous films was examined by porosimetry via ellipsometry and transmission electron microscopy. A design of experiment (DOE) method was used to gather information about the influence of the processing parameters on the final film structure. A model was developed, allowing a precise control of the pore diameters and porosity of the silica coating.

1. Introduction

Since the first templating approaches with supramolecular aggregates (lyotropic liquid crystalline phases) of periodically organized, mesoporous metal oxides by Kresge and Beck [1,2] the number of annual publications on this topic has increased every year. A lot of effort has been invested to get a precise control over the materials structures, e.g. pH-value was varied, different surfactants have been used and variable condensable precursors were applied to achieve a lamellar, hexagonal or cubic orientation of the pore system [3–6].

In 1991, Nakanishi and Soga [7] started to study the influence of different processing parameters on meso/macroporous structures prepared from tetraethoxysilane (TEOS) in the presence of a polymeric templating agent. The molar weight and concentration of the applied polymer, e.g. polyacrylic acid, were varied and the dependence on the average domain size was measured by scanning electron microscopy (SEM). These investigations were continued with different processing parameters and various templating agents resulting in pool of general recipes for the preparation of meso/macroporous metal oxides [8]. Templating techniques have not only been used to introduce porosity into SiO_2-Systems [9], TiO_2- [10] and ZnO-Systems [11] have also been investigated. A variety of templating agents like allylamine hydrochloride [12], PMMA [13] and acrylic polymers [14] are known to introduce characteristic, mainly macroscopic, pore structures.

Poly(ethyleneglycol) (PEG)/SiO_2-systems [15,16] have been reported to generate mesoporous materials, but, to our knowledge, the polymer-induced phase separation has not been systematically investigated for this material category. Our aim in this work was to produce a mesoporous material system prepared from TEOS and PEG and give basic instructions and guidance for the preparation of a controlled porosity and pore size. These materials become more and more important because of their optical or catalytic properties. This work was supported by using a "design of experiment"-method to optimize the experiment evaluation and interpretation of the results. This powerful methodology bringing a quantitative relationship between experimental and output parameters has rarely been used in correlation with sol–gel-based material systems up to now [17,18].

2. Experimental

All samples were prepared from TEOS as a silica source. A variable amount of PEG with different molecular weights was ultrasonically dissolved in a solution of 32 g ethanol, 1.4 g distilled water and 0.1 g 1 M HCl at a temperature of 40 °C. In case of high PEG amounts water was added dropwise (after 1 h of sonification) until the polymer was completely dissolved. After cooling the mixture to room temperature, it was added to a solution of 4 g

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doi:10.1016/j.apsusc.2009.04.043

TEOS in 8 g ethanol while stirring. The solution was covered and continuously stirred under ambient conditions.

Silicon wafers were used as substrates without any further precleaning. The coating was applied via dipping (100 mm min^{-1}) and subsequently, after having dried on air, cured at 400 °C for 30 min.

Samples with 27 different parameter sets were characterized using ellipsometry (Sentech SE 800) and porosimetry via ellisometry (Sopra EP 12) in order to determine the porosity, size of the pores and the refractive index. The porosity measured via toluene sorption was counterchecked with the one calculated from the refractive indices by a rule of mixture. The measured pore diameters were cross-checked by transmission electron microscopy.

3. Results

All coatings prepared were homogenous and crack free. A typical coating thickness was in the range of 80–300 nm.

Using the DOE-software "Design Expert 7" a model was set up, giving detailed information on the relation of the structure on the PEG-parameters, such as molecular weight and concentration, used. This model describing the dependency of the refractive index n of the silica layer on the templating parameters is shown in the equation below:

$$n = 4.34E - 3A^2 - 0.064A - 4.65E - 4AB + 2.96E - 3B + 1.38 \quad (1)$$

with A = polymer amount [%] and B = molar weight [1000].

According to Fig. 1 and Eq. (1), the amount of templating agent added to the solution is the main factor influencing the refractive index. The more polymer present in the coating solution, the lower the refractive index of the coating. Besides a quadratic influence of the polymer amount there is also a factor interaction between polymer amount A and molar weight B. The model calculated from the measured porosity values is shown in Fig. 2. Compared to the refractive index graph the trend and shape of the curves are in opposite direction. The determining factor for porosity is the amount of polymer in the solution.

Using this material system, depending on the polymer parameters, refractive indices as low as 1.10 and porosities above 70% are adjustable.

For the pore-size the following model was determined:

$$\text{pore size[nm]} = 0.576A + 0.031AB + 0.031B - 0.908 \quad (2)$$

with A = polymer amount [%] and B = molar weight [1000].

The plot of the pore size, resulting from these parameters, is shown in Fig. 3. An increase in one of the parameters A and/or B results in a linear increase of pore size. The TEM images taken at different points of the examined parameter area show the various pore geometries.

As a newly developed characterization tool (porosimetry via ellipsometry) was used to measure these values, TEM images of silica layers with different templating polymers (concentration and molecular weight) were taken and evaluated regarding their pore size.

These values were compared with values measured with the new tool (Fig. 4). It was found that both analytical techniques gave comparable values (within the errors of the different techniques). Both methods do not deliver absolute values but a trend. At the moment, the deviation between the two techniques cannot be explained.

This increase in pore-diameter, when adding more PEG, is possibly caused by higher degree of aggregation of the polymer molecules during the phase separation. The higher the concentration of the templating agent in the solution, the earlier the nano-demixing occurs. The polymer spheres grow larger until the silica network solidifies and limits the domain growth. As a result, there is a defined timeframe for the PEG domains to grow. If PEG-seeding starts early, the timeframe is extended.

Secondly the process is strongly depending on diffusion speed. If the polymer is present in higher concentrations, the diffusion paths become shorter and domain growth accelerates. These considerations also apply to the influence of the increase of the molecular weight of the PEG. As longer PEG chains are less soluble, seeding may occur earlier. The time-slot for the polymer aggregation is increased.

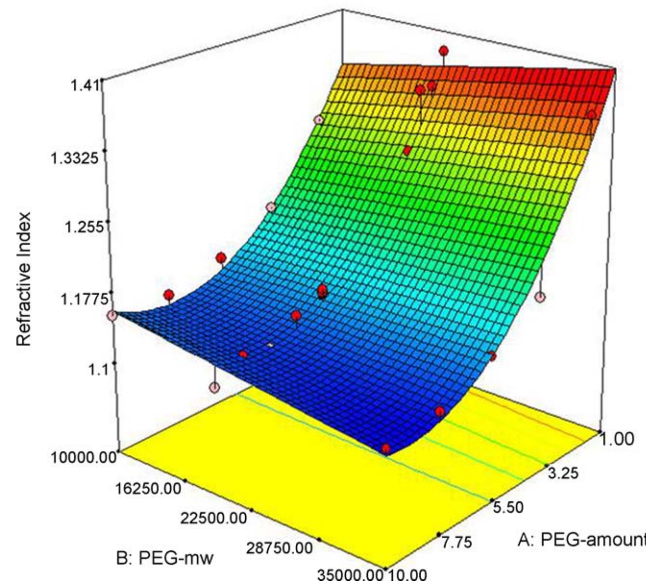

Fig. 1. Refractive indices of different silica layers resulting from a given molecular weight and a concentration of the templating polymer.

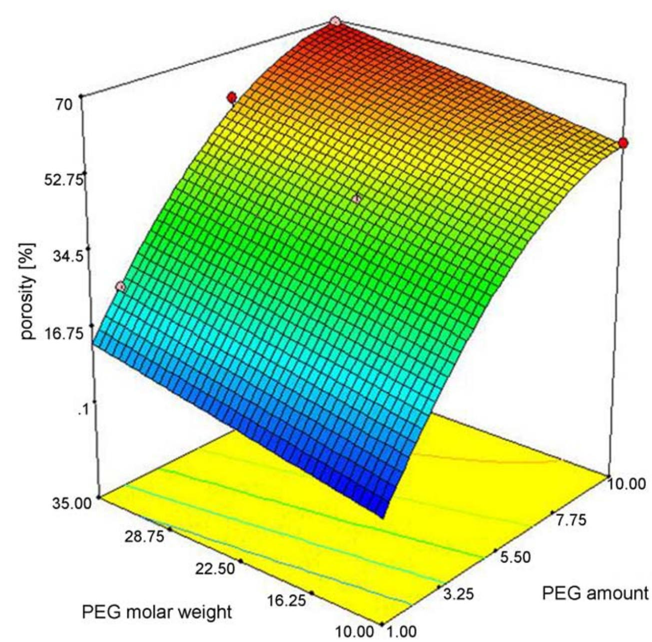

Fig. 2. Porosity of silica layers resulting from a certain molecular weight and a chosen concentration of the templating polymer.