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# Mesoporous silica thin films for alcohol sensors

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## Abstract

Silica mesoporous films using cetyltrimethylammonium bromide surfactant as a template have been prepared. The films have been deposited on silicon and alumina substrates by dip-coating and calcined at 250 and 450°C. The films were characterized by X-ray diffraction analysis, Fourier transform infrared spectroscopy and Rutherford backscattering spectrometry. The films have been shown to maintain the mesophase after calcination, at 250°C the presence of residual surfactant has been observed. A density of 1.46 and 1.65 g $cm^{-3}$ has been measured by Rutherford backscattering spectrometry in the 250 and 450°C calcined samples, respectively. These densities are much lower than the value (2.07 g $cm^{-3}$) measured in a reference silica film obtained via sol–gel and with the same thermal history. The electrical response of the silica mesoporous films has been investigated with different concentrations of alcohols. The sensitivity of the material to changes in the atmospheres of ethanol, methanol, 2-propanol, butanol-1 and exane has been tested. The results have shown a large sensitivity to the alcohols at room temperature and the possibility to discriminate between the different alcoholic species. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Films; Sensors; $SiO_2$; Sol–gel processes

## 1. Introduction

Several types of mesoporous materials[1–4] have been synthesized in recent years starting from the discover of MCM 41,[5,6] mesoporous films, in particular, are expected to have important technological applications in catalysis,[7] optoelectronics,[8] as sensors.[9] Many efforts are, therefore, focused on the synthesis of mesostructured materials in the form of thin films whose properties, such as pore sizes and shapes and accessibility to the porosity from the external environment, can be fully controlled. Different routes have been used to fabricate supported and unsupported mesoporous films.[10–20] Some simple sol–gel synthesis, in particular, has been developed for the fabrication of supported silica films.[15–20]

Lamellar[15] and hexagonal[16] mesoporous silica thin films on glass substrates by spin-coating have been deposited by Ogawa. A silicon alkoxide, tetramethoxysilane, has been prehydrolized in acidic conditions before the addition of a cationic surfactant, cetyltrimethylammonium bromide to form the organic template. The silica films, after calcination at 450°C, mantained their mesophase.

A similar route has been also used by Lu et al.[17] to deposit continuous mesoporous silica thin films on a solid substrate by dip-coating. A cubic mesoporous film, where the pores are connected in a three-dimensional network that gives access from the film surface, has been obtained.

Molecular templating by a cationic surfactant in a sol–gel process, similar to the previous one, has also been used by Berquier et al.[18] to obtain crack free transparent periodic mesoporous silica thin films. A quite different approach has been used instead used by Zhao et al.[19] who synthesized continuous mesoporous silica films with highly ordered and oriented periodic mesostructures. The mesoporous silica films have been obtained by dip-coating on glass and silicon substrates and preserved the mesostructure after calcination at 450°C. The materials have been prepared adding an ethanolic solution of a triblock copolymer or alkyl poly

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(ethylene oxide) oligomeric non-ionic surfactants to acid catalyzed silica sols.

A key point for technological applications of mesoporous films is represented by the accessibility of the mesophase from the external environment. The material should also exhibit a selective and reversible response to different species, as such alcohols or other different organic compounds. In this paper we have tested the capability of mesoporous silica thin films, prepared via sol–gel self-assembling processing, as alcohol sensors.

## 2. Experimental

The precursor solution was prepared in four steps using cetyltrimethylammonium bromide (CTB) (Aldrich) as the cationic surfactant. The other reagents were TEOS, $H_2O$, EtOH and HCl.

In the first step, TEOS was hydrolyzed under reflux at 60°C for 90 min, the molar ratios of the reagents were: TEOS:$H_2O$:EtOH:HCl = 1:7:3:0.04 (pH = 2). In the second step was added $H_2O$ to have the TEOS:$H_2O$ = 1:7.5 molar ratios and the sol was reacted under stirring 15 min at 50°C. After this step the solution was diluted with ethanol to reach the final molar ratios TEOS:EtOH = 1:22. In the last step CTB was added. The molar ratios were: $H_2O$:CTB = 7.5:0.1. Coating films were deposited by dip-coating on polished (100) silicon and alumina substrates. The samples were prepared in a humidity controlled box, with a withdrawal speed of 61.7 cm min$^{-1}$ and a 37% relative humidity. After the preparation, the films were calcined in air for 15 min at 250 and 450°C.

X-ray diffraction spectra were recorded on a Philips PW140 diffractometer with Ni-filtered Cu$K_\alpha$ radiation ($\lambda = 1.5418$ Å). A gracing angle geometry for thin film analysis was used. The following parameters were used: 40 kV and 50 mA, a 0.02° step, a counting time of 5 s, and an incidence angle of 0.5°.

Fourier transformed infrared (FTIR) absorption spectra, in the range 4500–400 cm$^{-1}$, were recorded by a Perkin Elmer 2000 spectrophotometer. The spectra were obtained from the films deposited on silicon substrate with a resolution of $\pm 1$ cm$^{-1}$.

The elemental composition of the samples was determined by means of Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA). A detailed description of these techniques and analysis conditions is reported in Ref. 21.

Thin mesoporous silica films were deposited by dip-coating on alumina substrates for electrical measurements. Electrical characterizations were done on mesoporous silica films dip-coated on alumina substrates where gold interdigitated electrodes were previously defined by photolithography. All the measurements were performed in dark conditions and at room temperature in a testing cell with a working volume of 40 cc.

Current measurements were done in environments containing different kinds of alcohol vapors. Ethanol, methanol, 2-propanol, butanol-1 and exane were the alcohols employed for the test. Alcohol vapours were produced by goggling a stream of nitrogen in a bottle containing the alcohol to be measured and mixing it with another dry nitrogen stream to change the relative vapor concentration. The mixing procedure was obtained by a MKS mass flow controller (total flow rate = 200 Standard Cubic Centimeter Minute (SCCM)). Current variations were measured with a fixed applied voltage (3 Volt) using the two points method. The measurements were done at 23°C.

## 3. Results and discussion

The small angle XRD patterns of the samples as deposited [pattern (a)], calcined at 250 [pattern (b)] and 450°C [pattern (c)] are shown in Fig. 1. A main broad peak around 3° in $2\theta$, attributed to the formation of a mesophase,[10,16,17] is observed. The peak shifts to larger values in $2\theta$ while the intensity between uncalcined and 450°C calcined samples does not change. The $d$ value shows a reduction of around 11%, from 3.95 to 3.38 nm after calcination at 450°C, this is due to the shrinkage of the structure upon calcination.

Fig. 2 shows the FTIR absorption spectra in the range 4000–450 cm$^{-1}$ of as deposited (a), 250 (b) and 450°C calcined samples. Typical bands of silica gels films are found in the spectra.[22] The three main peaks characteristic of silica films are detected at around 1070, 800 and 460 cm$^{-1}$ in all the samples. The band around 930 cm$^{-1}$ is attributed to the presence of Si–OH or S–O$^-$ species.[22] This band decreases in intensity after calcination but is still clearly observed in the 450°C calcined samples.

The as deposited and 250°C calcined spectra show a wide O–H stretching band around 3400 cm$^{-1}$, due to freely vibrating OH groups and hydrogen-bonded OH groups.[22] This band decreases in intensity during calcination.

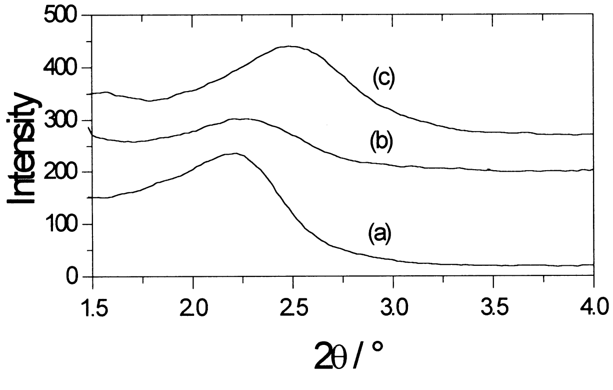

Fig. 1. XRD pattern of the mesoporous silica films deposited on silicon substrates: (a) as deposited films; (b) 250°C calcined films; (c) 450°C calcined films.

In the as deposited and 250°C calcined films some absorption bands are observed in the region 2800–3000 cm$^{-1}$ and attributed to or CTB surfactants.[23] CTB FTIR spectra show two intense bands, assigned to asymmetric (~2980 cm$^{-1}$) and symmetric (~2850 cm$^{-1}$) stretching vibrations of C–$CH_2$ in the methylene chain.[23] Several weak bands detected in the region of 2940–2960 cm$^{-1}$ are assigned to C–$CH_3$ asymmetric stretching and N–$CH_3$ symmetric stretching vibrations of solid surfactant. The XRD patterns, however, did not reveal any peak that could be directly correlated to crystalline CTB in the films, differently from what was found in Refs. 2 and 4. In our case the amount of solid CTB is at least too small to be detected by XRD analysis.

The absorption energies of $CH_2$ stretching vibrations are considered to be related with the physical state (monomer, micelle or solid) of the surfactant (see Ref. 23 and references therein). In our work the $CH_2$ vibrational energies are found at 2855 and 2925 cm$^{-1}$, indicating that the surfactant is present in the film as micelles.

The composition and the density of the mesoporous films calcined at 250 and 450°C are reported in Table 1. The composition and density of a silica sol–gel film, used as a reference, are also reported. The density of the mesoporous films is much lower than in the silica film. The content of hydrogen is larger in the mesoporous films than in the $SiO_2$ reference film and decreases with increasing the calcination temperature. In fact, as already found in the FTIR spectra, the amount of OH groups in the mesoporous films is quite high, even in the film calcined at 450°C. The presence of Br in the mesoporous films heated at 250°C is in agreement with the FTIR spectra (Fig. 2) that show the presence of residual surfactant up to 250°C. The content of C is almost the same for all the calcination temperatures. This can be due to the not hydrolysed OR groups, which are not yet decomposed and/or to the surfactant.

Figs. 3–6 show the electrical response of the mesoporous silica films when exposed to ethanol (Fig. 3), methanol (Fig. 4), butanol-1 (Fig. 5) or 2-propanol (Fig. 6) vapours. The films did not show, instead, any response after exposition to exane vapours (not shown in the figures). The films exhibited a different response to the alcoholic vapours as a function of the calcination temperatures. The samples calcined at 250°C show, in general, a more sensitive response with the exception of the case of butanol-1 vapours. This difference is due to the changes in porosity produced during calcination, with a reduction of around 15% in porosity between the samples treated at 250 and 450°C. Another effect is also due to the presence of the residual surfactant within the pores that will affect the absorption of the different

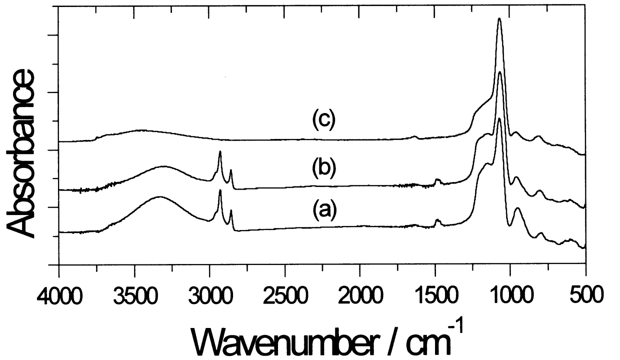

Fig. 2. FTIR spectra of the mesoporous silica films deposited on silicon substrates: (a) as deposited films; (b) 250°C calcined films; (c) 450°C calcined films.

Table 1
Composition (at.%) and density of the films measured from the RBS analysis. $SiO_2$ = silica sol–gel reference film, MES = mesoporous silica films

| Sample | Composition | | | | | Density |
|---|---|---|---|---|---|---|
| | Si | O | C | Br | H | $\rho$ (g cm$^{-3}$) |
| $SiO_2$ (450°C) | 26.5 | 57.5 | 8.8 | – | 7.2 | 2.07 |
| MES (450°C) | 18.8 | 48.7 | 7.5 | – | 25.0 | 1.65 |
| MES (250°C) | 12.0 | 41.0 | 6.0 | 1.0 | 40.0 | 1.46 |

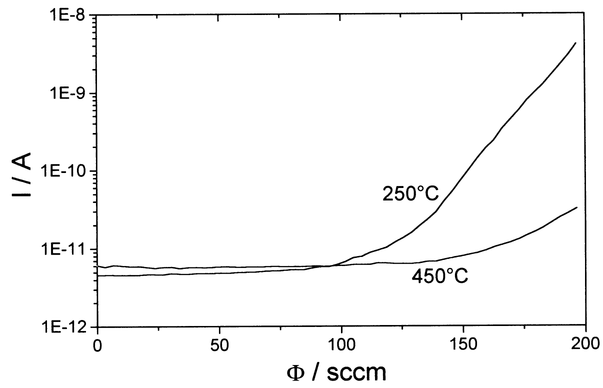

Fig. 3. Current intensity in the films as a function of ethanol stream flux in the measurement room. $V_{pol}$ = 3 V, $T$ = 23°C.

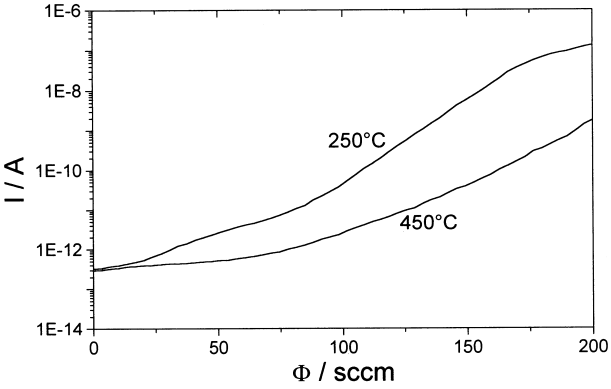

Fig. 4. Current intensity in the films as a function of methanol stream flux in the measurement room. $V_{pol}$ = 3 V, $T$ = 23°C.

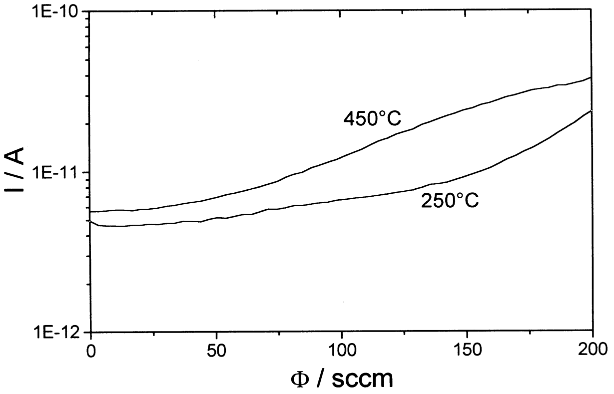

Fig. 5. Current intensity in the films as a function of butanol-1 stream flux in the measurement room. $V_{\text{pol}}=3$ V, $T=23°\text{C}$.

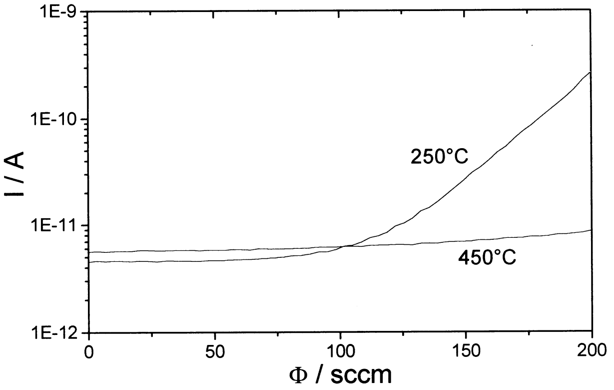

Fig. 6. Current intensity in the films as a function of 2-propanol stream flux in the measurement room. $V_{\text{pol}}=3$ V, $T=23°\text{C}$.

alcoholic species. All the samples show a larger sensitivity at higher vapour concentrations, the electrical response is, generally, observed to start over $\Phi=100$ sccm. Interestingly the samples show a quite different response to the different alcohols suggesting a possible application for the fabrication of a selective sensor.

## 4. Conclusions

Mesoporous silica thin films prepared via a self-assembling process using cetyltrimethylammonium bromide as surfactant template have been tested as alcohol sensors. The films have shown a sensitive response to different alcohol vapours and the response has changed with the alcoholic species used in the test. A different response has as a function of the calcinations temperature has been also observed.

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