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Humidity sensors based on mesoporous silica thin films synthesised by block copolymers

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Abstract

The application of mesostructured thin films to fabricate electrochemical sensors requires the control of dimension, shape and distribution of pores in the material. Silica mesoporous thin films were deposited via dip coating on silicon and alumina substrates with interdigitated electrodes. Mesostructured films were obtained by sol-gel self-assembled process using di-block, tri-block or star-block copolymers: 2-D hexagonal mesoporous phases in silica were formed. After deposition the films were calcined in air to remove the surfactant and were characterised by Fourier transform infrared spectroscopy and low angle X-ray diffraction. Current variations with relative humidity were measured using different applied d.c. voltage; I/V characteristics were performed at various relative humidity values. Moreover the dependence of response from temperature and behaviour during cyclic test in dry–wet conditions was studied. The electrical response was found to be dependent on dimension of pores and their surface. Electrical characterisation upon exposure to humidity shows that the mesoporous structure is easily accessible by external environment, and the films prepared by non-ionic surfactants exhibit good performances in comparison with commercial humidity sensors.

Keywords: Electrical properties; Mesostructure; Porosity; Sensors; Sol-gel processes

1. Introduction

Many scientific and technological efforts to develop gas sensor devices are focused on improving their overall properties. New generation gas sensors, in fact, should exhibit a wide operation range temperature, high temporal stability, good accuracy, small hysteresis loop, low price, easy processing and reproducibility and a wide concentration sensing range. Mesostructured thin films, because of their high specific area (which can be as high as 500–1000 $cm^2\ g^{-1}$), the high porosity and the organization of the material, have recently attracted some interest as materials for sensing applications, electrochemical[1,2] or optical devices.[3] The controlled accessibility of porosity from external environment and chemical species on the pore surface area may allow, in fact, the maximization of the response to external changes to reach a greater sensing selectivity.

To direct the formation of the mesostructure in the films, non-ionic amphiphilic block copolymers[4,5] or ionic surfactants[6–8] are currently used. Block copolymers, in particular are commercially available in the market, are not expensive and easily removed from the matrix. The self-assembled structures directed by non-ionic block copolymers can give rise to different mesophases according to the effective concentration of copolymer in solution. Cubic, hexagonal or lamellar mesophases can be obtained controlling the concentration.[9] The dimension of the pore can be controlled using different types of block copolymers.[10] Removal of the copolymer can be obtained via calcination, chemical extraction or selective UV photocalcination.[11] After calcination mesoporous films with porosities within the range of 10–50 nm and ordered distribution of the pores are obtained. Porosity forms an ordered structure analogous to the copolymer mesophase.

An important property of mesoporous films for their practical sensing applications is the accessibility from the external environment of the mesophase, which has a large interfacial area. In fact, at the surface of mesoporous film

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the ordered configuration of adsorbed water molecules from the air promotes the protonic conduction that is outlined by the "Grottus model".

2. Experimental

The synthesis of the precursor solution was done at room temperature using different types of non-ionic surfactants as structure-directing agents: two-block linear (Brij), three-block linear (Pluronic) and star copolymer (Tween). Two different separate solutions were prepared. The first one called *stock solution* was prepared by mixing tetraethylorthosilicate (TEOS), ethanol (EtOH), H_2O and HCl. The second one called *templating solution* contained the surfactant (Brij-58, Pluronic F-127, Tween-80), EtOH and a weakly acid aqueous solution (HCl). The stock solution was stirred for 1–2 h to allow the hydrolysis of the silane units and then added to the templating solution. After 1–2 days under magnetic stirring at room temperature the final solution was aged for another 5–8 days.

The film was deposited via dip coating on substrates maintaining the RH% in the deposition chamber in the range 25 – 40% and temperature at 25 °C. The withdrawal speed was set at 20 cm min^{-1}. The surfactant concentration was fixed at 5.5 wt.% of the final solution for the linear block surfactants (Brij and Pluronic), at 15 wt.% for star block copolymer (Tween). The samples were finally calcined in air at 350 °C for 40 min.

To evaluate the degree of order, low angle X-ray diffraction (LAXRD) was used. The microstructural evolution of the films during thermal treatment up to a complete loss of the organic phase, was observed by Fourier transformed infrared spectroscopy (FTIR).

The devices used to perform the electrical characterisations were prepared using both Al_2O_3 and silica on silicon substrates. Interdigital electrodes, gold and chromium 200 nm thick, were photolithographically defined with different geometry: eight fingers 280 μm wide and spaced 120 μm for alumina substrates, 40 fingers 20 μm wide and spaced 20 μm for silicon substrates. The electrode lengths were 4500 μm for alumina substrates and 5640 μm for silicon substrates. The electrical response of the devices was analysed by d.c. and a.c. measurements in a dark condition in a suitable cell where both temperature and humidity were monitored. Relative humidity was measured using a commercial sensor (Honeywell HIH 3602 C), which gave an accuracy of ±1%. The current response due to RH variations (from 5 to 95%) for different values of applied voltage at the electrodes were recorded. Relative humidity has been changed with a step of 2.5% every 100 s (T_s).

In order to evaluate both the resistive and capacitive parameters on frequency domain, electrical impedance spectroscopy (E.I.S.) measurements were performed.

3. Results and discussion

LAXRD spectra showed that the silica mesoporous films have an ordered pore distribution (Fig. 1), the degree of order and the interplanar distance clearly decreases with the thermal treatment of the sample. Moreover, we certainly have a normal shrinkage of the lattice symmetry: calcination modifies the structure from 2-D hexagonal to 2-D centred rectangular. The effective conversion of the film from mesophasic to mesoporous material has been observed by FT-IR spectroscopy. After the treatment at 350 °C the absorption bands related to C–H mode of copolymer in the range 2700 – 3000 cm^{-1} were absent (Fig. 2) confirming the complete removal of the copolymer from the samples.

Measurements performed on alumina substrates upon d.c. voltage application have shown large current variations (up to four order of magnitude) related to exposure in a humid environment. Similar behaviour has been obtained for the films on silica on silicon substrates. If we compare the dependence from the RH of

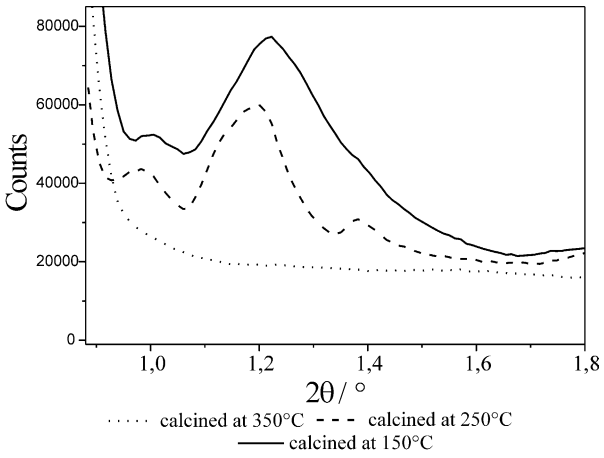

Fig. 1. Low angle XRD patterns of silica mesoporous films obtained with Pluronic F-127 (X-ray source: CuK_α).

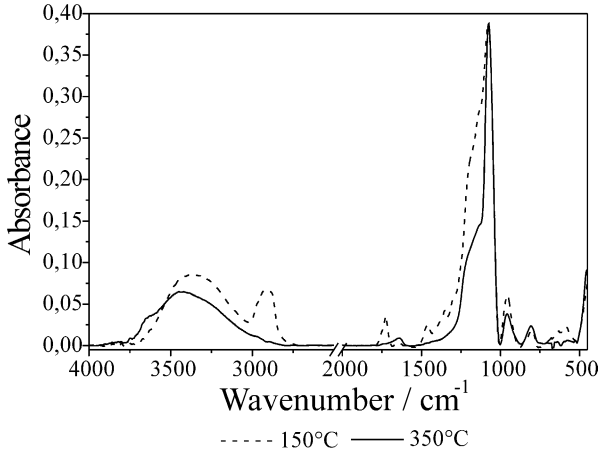

Fig. 2. FTIR absorption spectra of silica mesoporous films obtained with Pluronic F-127 after calcination at 150 and 350 °C for 1 h.

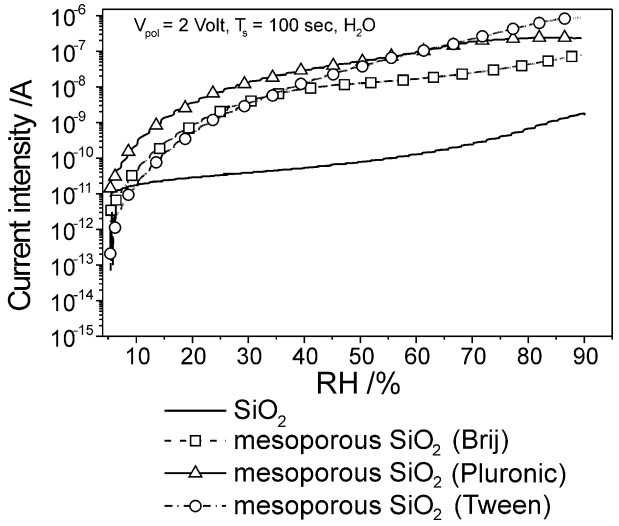

Fig. 3. Electrical response vs. RH variation as a function of the different block copolymers used for the synthesis of mesoporous silica films (operating temperature: 24.7 °C).

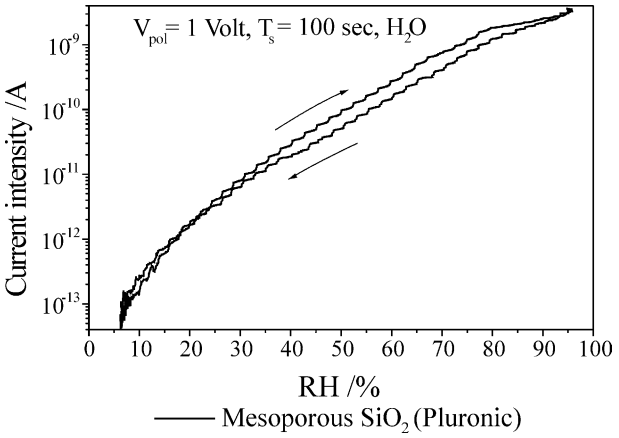

Fig. 4. Hysteresis loop in the response of the sensor device (silica mesoporous films from Pluronic, operating temperature: 26.2 °C).

Table 1
Comparison of the resistance and capacitance values measured by impedance spectroscopy in silica sol-gel films (SiO_2) and mesoporous silica films prepared by Brij-58, Pluronic F-127, Tween-80

	Resistance / Ω	Capacitance / F
SiO_2	$2.3 \cdot 10^{10}$	$8.9 \cdot 10^{-12}$
Brij	$7.6 \cdot 10^{7}$	$9.3 \cdot 10^{-12}$
Pluronic	$4.4 \cdot 10^{7}$	$9.6 \cdot 10^{-12}$
Tween	$8.4 \cdot 10^{7}$	$8.4 \cdot 10^{-12}$

the steady state current response with that of a silica sol-gel film (Fig. 3), which is actually not mesoporous, we can observe a more sensitive region of the response curve for low humidity concentrations that is attributed to the large amount of porosity and surface area in the mesostructured films. The large porosity produces a highly active surface, covered of silanol species (Fig. 2)

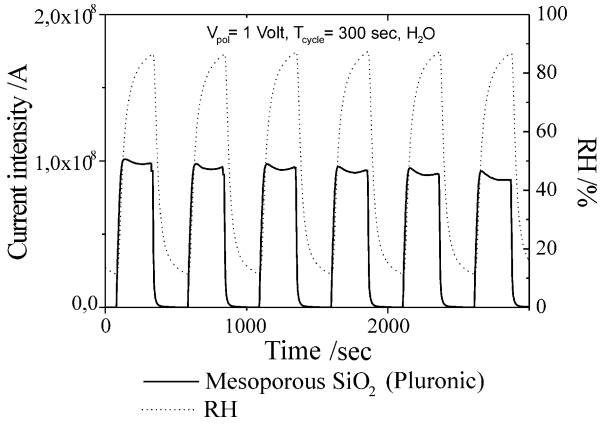

Fig. 5. ON/OFF cycles to test the stability of the device response (silica mesoporous films from Pluronic).

absorbing water molecules and increasing the current intensity related to the protonic conduction: hence the reference silica samples have exhibited only a very weak response modification upon changes of the humidity environment, whereas large responses are observed in the mesostructured films. Samples prepared by different block copolymers show some differences in the response, which are however difficult to correlate, at the moment, with microstructural differences because of the many parameters that can affect the performances of the materials such as for instance differences in pore dimension, overall porosity, pore accessibility, silanols species on the pore surface, and the presence of micropores in the silica walls. It is interesting to observe that samples produced by tri-block copolymers show a larger reproducibility of the sensing response and almost no hysteresis. The little hysteresis loop between the electrical response recorded increasing and reducing the RH value (Fig. 4) in Pluronic derived mesoporous films is probably related to polarization phenomena in the samples. Preliminary E.I.S. measurements have emphasized the high resistance values of the devices and have also allowed to estimate their capacitance. The results of the measurements carried out at ambient temperature and maintaining the humidity at constant value (RH at 60%) are reported in Table 1.

ON/OFF cycles in dry and wet atmospheres have been performed to test the stability as a function of operating time (Fig. 5). The devices show a response without significant memory effects increasing the number of working cycles. Variations of electrical response appeared very quickly with the change of RH value in the chamber atmosphere.

4. Conclusions

Mesoporous silica thin film synthesised using supramolecular self-assembling with block-copolymers as

structuring agents have been tested as humidity sensors. The films have shown a very different sensitive response with respect to no-mesoporous silica sol-gel thin films used as reference in testing measurements. The mesophase is easily accessible by the external environment and increases the performances for sensing applications. A good reproducibility of the electrical response and a different response as function of the surfactant used as templating agent have been observed. The sensor device has also shown no memory effects after cyclic testing in dry–wet conditions.

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