

X-rays and electrical characterizations of ordered mesostructured silica thin films used as sensing membranes

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Abstract

Mesoporous silica (MPS) thin films were characterized by X-ray analysis and electrical measurements to investigate possible correlation between structural order and best response of this kind of sensing material toward RH and alcohols vapours. Both energy dispersive X-ray diffraction and X-ray reflectometry results have been discussed to describe the ordered porosity distribution in the amorphous film. A phenomenological trend of the resistive-type sensors response changing calcination has been found and related to the change in the porosity order of MPS thin film.

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1. Introduction

Sol–gel self-assembly process [1] is a simple chemical route to control the dimensions of mesophases in metal oxide powders and thin films. In particular, highly ordered mesostructured thin films with cationic surfactants [2] or non-ionic block copolymers [3] can be deposited by dip-coating on substrates. Cubic, hexagonal or lamellar mesophases can be obtained controlling the effective concentration in the precursor solution [4]. Non-ionic block copolymers are commercially available, not expensive and can be easier removed than ionic templating agents from the host matrix. Chemical extraction, thermal [5] or photo-calcination [6] are suitable treatments to remove the organic mesophase and to obtain mesoporous metal oxide thin films with highly ordered porosity and large specific area.

Mesostructured materials, because of their properties, have potential applications for sensing, electrochemical and optical devices. Resistive sensor devices based on meso-

porous silica thin film as sensing membrane have been developed to detect both humidity and alcohol vapours in environment [7]. The performance of the sensors has been found to be dependent on the film preparation method, especially on the calcination temperature and its lasting. Indeed, thermal treatments modify both the silica and the pore structure, therefore the sensing material structural changes could justify the electrical sensor response modifications observed in testing experiments. Aim of this work is the examination and a better understating of this supposed correlation.

2. Experimental

Electrical sensor devices has been made by a mesoporous silica thin film deposited by dip-coating on Si/SiO₂ substrates where chromium interdigitated electrodes have been previously evaporated and photo-lithographically defined. Electrodes geometry is 2000 Å thick, 20 μm wide and distance between fingers is 20 μm. Films have been deposited in controlled humidity and temperature conditions and finally calcined. Sensor device testing has been obtained introducing

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it into a chamber of 40 cm³ working volume. Using a MKS mass flow controller in the range from 0 to 200 standard cubic centimetre per minute (SCCM) dry and wet nitrogen stream with a constant 200 SCCM total flow rate has been introduced into the cell to obtain relative humidity variation from 5 to 90%. The electrical response of the resistive-type sensors has been evaluated measuring the current intensity values towards RH% variation. All measurements were performed in dark condition to prevent possible undesirable photo-assisted phenomena. The current was detected using a Keithley 595 Quasistatic CV meter, which assures a resolution of $\pm 5 \times 10^{-15}$ A. Current variations were measured with a fixed applied voltage (1 V) using the two points method. Temperature was recorded and maintained at a constant value of 25 ± 1 °C.

X-ray diffraction experiments were carried out by using an EDXD apparatus elsewhere describe [8,9]. The intensity distribution scattered by mesoporous material is function of the module of the momentum transfer q expressed as a function of the wavelength of the incident radiation λ and the scattering angle θ by relation: $q = (2\pi \sin \theta)/\lambda$.

The X-ray reflectometry is a technique sensitive to surface and interface morphology at the Ångstrom resolution and is commonly utilized to probe the properties of surfaces and interfaces of layered samples (films deposited on substrates, multilayers, superlattices, etc.).

The method makes use of the optical properties of X-rays briefly outlined in the following and fully reported elsewhere [10].

In optics, referring to the film surface, the Snell law can be expressed as $n_1 \cos \theta_1 = n_2 \cos \theta_2$ (θ_1 and n_1 being the incidence angle of the primary beam and the refractive index of the first medium, and θ_2 and n_2 being the reflection angle and the refractive index of the second medium). If the first medium is vacuum (or air), $n_1 = 1$ and the previous equation, at the critical angle θ_c , takes the form: $\cos \theta_c = n_2$, since when $\theta_1 = \theta_c$, $\theta_2 = 0$.

In the X-ray energy range, the refractive index can be expressed as:

$$n = 1 - \left(\frac{\lambda^2}{2\pi}\right) \rho r_0 Z^2 + i \left(\frac{\lambda}{4\pi}\right) \mu$$

where λ being the incident wavelength, ρ the material density, r_0 the classical electron radius, Z the atomic number and μ is the linear absorption coefficient, typically 10^{-6} to 10^{-7} , thus negligible.

Therefore, the total reflection conditions are fulfilled when $\cos(\theta_c) = 1 - (\lambda^2/2\pi)\rho r_0 Z^2$ that, at the second-order approximation, can be summarized as $q_c = \theta_c/\lambda = \text{constant}$, where q_c is the critical scattering parameter (momentum transfer). The q range of interest, containing all the morphological information, is around this critical value.

Indeed, the position of the critical edge (q_c) and the slope of the reflectivity profile are determined by the material density and the surface roughness (variance from the

average thickness), respectively. Furthermore, if the sample consists of a thin film deposited on a thick substrate, the signal exhibits oscillations produced by the interference of the two waves reflected at the surface and interface: the frequency of the oscillations is roughly proportional to the film thickness, while their damping is related to the interface roughness.

To collect an X-ray reflection spectrum, that is the reflected intensity as a function of q , two ways can be used. In fact, the q scan can be accomplished either by utilizing a monochromatic beam and an carrying out an angular scan (angular dispersive mode) or using a polychromatic X-ray beam at fixed angle and carrying out an energy scan [energy dispersive (ED) mode], no movement being required [11].

The advantages of the ED technique on the angular dispersive counterpart, mainly related to the immobility of the experimental setup, are particularly remarkable when reflectometry measurements are concerned [12,13]. Indeed, in the ED mode, a single spectrum collected at fixed angle which covers a range of some 10^{-1} Å⁻¹, is made of a collection of several hundred points so that the q -resolution approaches 10^{-4} Å⁻¹. Such q -resolution would be hardly achieved using a conventional laboratory angular dispersive reflectometer. Moreover, the stationarity of the experimental setup reduces the systematic errors induced by the angular scan (misalignments and aberrations) and guarantees the reproducibility of the experimental conditions (particularly critical at small angles) when many consecutive measurements have to be performed, as in the present case. This allows to perform in situ investigations with an extremely high level of confidence. On the other hand, the main drawback of the ED mode, i.e. the decrease in the q -resolution due to the uncertainties on both the angle and the energy, does not affect a reflectivity measurement since the EDXR pattern of a thin film is characterized by long period oscillations.

The energy dispersive X-ray reflectometer used is a non-commercial machine [14]. The instrument is provided with two benches, one carrying the X-ray tube, the other the energy sensitive detector, pivoting around a single central axis. The X-ray optical path is defined by four variable slits mounted on the arms. The arms are moved by two linear actuators driven by step motors and the tangent of the angle is read by two linear encoders. Both the minimum step movement and the resolution are of the encoders are 1 μm, that, in our case, guarantees a reproducible minimum angle increment of 0.004°. The white incident beam is produced by a standard 2 kW tungsten anode X-ray tube and the detection is accomplished by an EG&G high purity germanium solid-state detector. The detector is connected to a PC via ADCAM hardware and the signal is processed by a Maestro software, which performs the necessary analogue to digital conversions. The energy resolution $\Delta E/E$ is ca. 1.5% in the energy range of interest (20–50 keV). Neither monochromator nor goniometer is required in the energy dispersive mode.

3. Results and discussion

The steady-state current response of the mesoporous silica films as a function of RH changes in the measurement chamber show different curves due to samples calcined at different temperatures. Each curve was recorded in a cycle of increasing and decreasing RH to evaluate the electrical response changes and the memory effects in the material. Two almost overlapped curves were observed in all the samples, indicating a very little hysteresis loop. The current intensity change was up to 5 orders of magnitude, in films calcined at 550 °C, for instance, the current increased from 5×10^{-12} A (9% RH) up to 8×10^{-7} A (92% RH). A good electrical response should be correlated to the formation of the “ice like” layers and the presence of water molecules with higher hydrogen bonding.

The curves of sensitivity [15] (first derivative of the current intensity versus RH) are shown in Fig. 1. The sensors exhibited an enhanced sensitivity with the increase of the RH, with a steady peaking around 70% RH. After this RH value the sensitivity quickly decreased and at RH larger than 85% the curves showed the tendency to saturate. The 550 °C calcined samples showed, however, a quite different behaviour, with a low sensitivity up to around 50% of RH and a constant increase in sensitivity at larger RH.

The relationship between the current intensity and the calcination temperature as a function of relative humidity is shown in Fig. 2. The curves were fitted by a Gaussian function. The larger absolute current values were observed for samples thermally treated at 350 and 450 °C. The films annealed at 550 °C showed the lowest current intensity response, which indicates a lower performance of the sensing device, at least in the considered range (30–70% RH).

We can note indeed that the template presence can enhance the current intensity at low RH value but, on the other hand, it leads to promote a saturation phenomenon and then to reduce the device sensitivity at higher RH value. Otherwise, the device calcined at 550 °C, even if its current intensity and selectivity are lower up to 70–80%

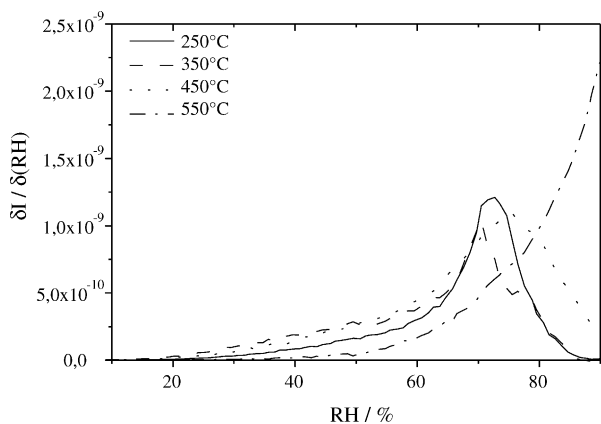


Fig. 1. Sensitivity curves have been obtained from the electrical characterizations vs. the relative humidity content.

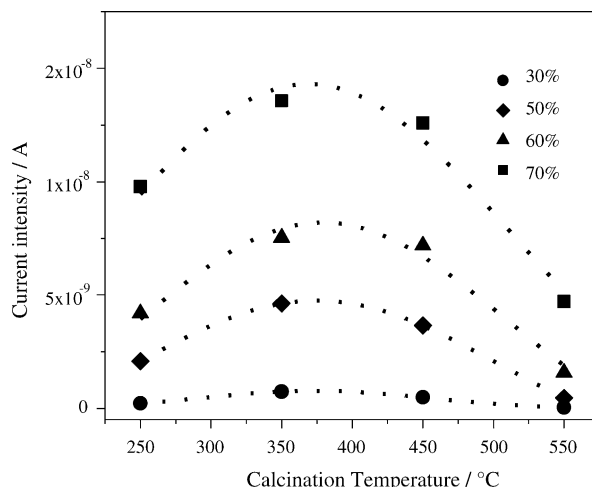


Fig. 2. The electrical behaviours of devices at fixed RH% values make possible an intensity responses comparison.

RH, it shows a better performance at higher humidity values.

All samples calcined at various temperatures in the range 150–1050 °C were tested. In Fig. 3, the EDXD spectra of the samples treated between 150 and 950 °C show an increase of the momentum transfer q , i.e. a decrease of the interplanar space $d = 2\pi/q$ (inset, Fig. 3) with increasing calcination temperature. The curve values in Fig. 3 were normalized. This shift of the main diffraction peak suggests that the material structure suffers a shrinkage. This shrinkage is homogeneous in each direction, in fact all the Bragg peak positions have the same trend as a function of temperature. In Fig. 4, we reported the D (Å) in state of momentum transfer q (Å⁻¹) as function of calcination temperature. We suppose that the temperature increase improve the copolymer removal and at the same time modifies the silica properties, causing a closing of the pores. A correlation with SAXS data, indicates that the cubic phase is the most probable structure. The relative peak positions are $\sqrt{4}$ and $\sqrt{8}$, the absence of other reflection peaks preventing to distinguish between a body-centre cubic phase or a face-centre cubic phase. The Miller indexes for the

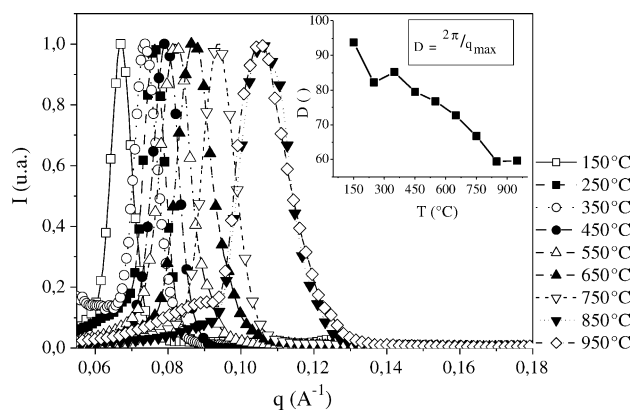


Fig. 3. The diffraction peaks in function of the q momentum and therefore of the interplanar space D are clearly visible in the EDXD spectra.

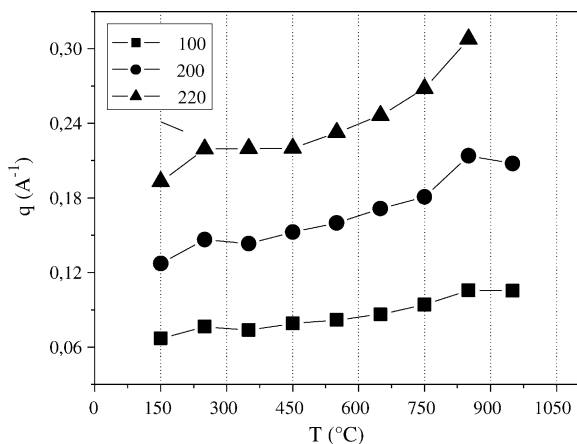


Fig. 4. Momentum transfer q (\AA^{-1}) from EDXD spectra as function of calcination temperature.

three reflections are (1 0 0), (2 0 0) and (2 2 0). The sample at $T = 1050^\circ\text{C}$ have not shown any Bragg peak, because the elevated temperature does not allow silica to evolve in a stable configuration, and the structure has a collapse destroying any ordered phase.

A systematic reflectivity analysis was performed in order to achieve morphological and long range structural information upon samples of these materials, calcinated at various temperatures in the range $150\text{--}1050^\circ\text{C}$.

All reflectivity patterns were collected in the same conditions, at grazing incidence ($\theta = 0.125^\circ$) and in a controlled atmosphere (N_2 flux, 180 nmol/s). Superlattice Bragg peaks are visible in the reflectivity spectra (Fig. 5), witnessing an internal order of the thin films. Indeed, since the reflected signal is due to the optical contrast between the scattering materials, such peaks can be attributed to the presence of an ordered porous structure inside the films. In particular, the reflection pattern of the sample calcinated at 150°C differs from those of the others, because it exhibits an anomalous (convolved) double peak. This can be attributed to the presence in the bulk of two ordered materials with different

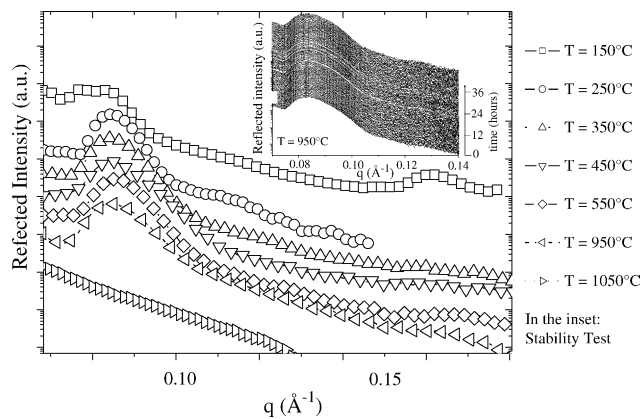


Fig. 5. X-ray reflectivity spectra are plotted as a function of the scattering parameter q , comparing the profiles upon different temperatures and a stability test upon the less ordered film is shown.

scattering length densities, the surfactant still being present at such low calcination temperatures. Indeed, as the temperature grows, only the signal coming from the mesoporous structure remains and the Bragg peaks get broader, indicating that the internal order is decreasing due to the thermal treatment. Finally, at 1050°C , reflections are no longer visible indicating the lack of the mesoporous structure order.

Surface roughness was calculated by the Parrat model for reflectivity profiles. All the films exhibit a roughness value in the range $6\text{--}8\text{ \AA}$, except for the one calcinated at 1050°C , whose value is as high as $13(2)\text{ \AA}$. This is another evidence confirming the disorder characterizing such high calcination temperature, not only in the bulk, but even on the surface.

The sample calcinated at 950°C is the last one to show a kind of internal structure, even though the reflection is now very weak and the Bragg peak is extremely broad. This sample, being the last that retains a certain degree of order, is the most critical and the following stability test was performed on it. The sample was submitted to alternate conditions, i.e. in the controlled atmosphere described above, then at room conditions (temperature, pressure and relative humidity), and finally under the controlled atmosphere, again. The residence time in such conditions was 12 h each. During the overall 36 h (Fig. 5), the sample was irradiated by an X-ray beam at grazing incidence and a sequence of 15 min long X-ray reflectivity spectra was collected. Passing from the N_2 gas flux to room conditions (and back), no variation was observed either in the peak position, in its shape or in the slope of the underlying reflectivity profile. This is an evidence that no morphological and structural modifications occur, namely that the film is stable even when left in air.

4. Conclusions

Humidity sensing devices based on mesoporous silica thin film have been fabricated via dip-coating. Their current response and sensitivity is dependent on the calcination temperature chosen in the sensor manufacture. Sensing material structure has been studied using energy dispersion X-ray techniques: diffraction and reflectivity spectra has been collected and examined for samples that have been treated at temperature in the $150\text{--}1050^\circ\text{C}$ range. Stability of the film structure in air has been observed. An interesting correlation between sensing properties and porosity or structural changes of silica has been observed.

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References

- [1] C.J. Brinker, Y. Lu, A. Sellinger, H. Fan, *Adv. Mater.* 11 (1999) 579.
- [2] M. Ogawa, *Supramol. Sci.* 5 (1998) 247.
- [3] G.J.A.A. Soller-Illia, C. Sanchez, B. Labeau, J. Patarin, *Chem. Rev.* 102 (2002) 4093.
- [4] P.C.A. Alberius, K.L. Frindell, R.C. Hayward, E.J. Kramer, G.D. Stucky, B.F. Chmelka, *Chem. Mater.* 14 (2002) 3284.
- [5] A. Stein, B.J. Melde, R.C. Schrodin, *Adv. Mater.* 12 (2000) 1403.
- [6] A. Hozumi, Y. Yokogawa, T. Kameyama, K. Hiraku, H. Sigimura, O. Takai, M. Okido, *Adv. Mater.* 12 (2001) 985.
- [7] J. Mio Bertolo, A. Bearzotti, P. Falcaro, E. Traversa, P. Innocenzi, *Sensor Lett.* 1 (2003) 64–70.
- [8] S.J. Roser, R. Felici, A. Eaglesham, *Langmuir* 10 (1994) 3853.
- [9] R. Caminiti, V. Rossi Albertini, *Int. Rev. Phys. Chem.* 18 (2) (1999) 263.
- [10] X.L. Zhou, S.H. Chen, Theoretical foundation of X-ray and neutron reflectometry, *Phys. Rep.* 257 (1995) 223–348.
- [11] A. Generosi, V. Rossi Albertini, G. Rossi, G. Pennesi, R. Caminiti, *J. Phys. Chem. B* 107 (2) (2003) 575–579.
- [12] K. Orita, T. Moritura, T. Horiuchi, K. Matsushige, *Synth. Met.* 91 (1997) 155–158.
- [13] V. Rossi Albertini, A. Generosi, B. Paci, P. Perfetti, G. Rossi, A. Capobianchi, R. Caminiti, *Appl. Phys. Lett.* 82 (22) (2003) 3868.
- [14] R. Caminiti, C. Sadun, V. Rossi Albertini, F. Colloco, Patent No. 01261484, Italy, 1993.
- [15] A. D'Amico, C. Di Natale, *IEEE Sens. J.* 1 (2001) 183–190.

Biographies

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Andrea Bearzotti, born in Udine, Italy, on October 19, 1960. He received the Laurea degree in “physics” from the University of Rome “La Sapienza” in February 27, 1986, with a thesis titled: “M.O.S. structure with palladium gate as hydrogen and oxygen sensor”.

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