

Sensing CO₂ in a chemically modified porous silicon film

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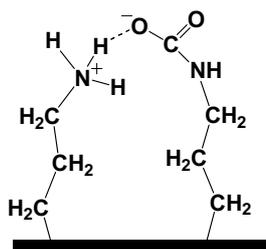
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An inexpensive and compact carbon dioxide sensor based on a porous silicon (PS) film modified with 3-amino-1-propanol has been demonstrated. The modifying reaction as well as the interaction of carbon dioxide with the PS amine-terminated surface has been investigated using Fourier Transform Infrared Spectroscopy. Optical reflectivity spectra of PS modified layers display shifts in the Fabry–Perot fringes upon adsorption of carbon dioxide. This shift scales with the CO₂ concentration.

1 Introduction There are two main types of carbon dioxide sensors: infrared absorption-based sensors and electrochemical sensors. The former use the fact that CO₂ absorbs strongly at 4.26 μm (2349 cm⁻¹) and its absorption is a function of the partial pressure of the gas. Non dispersive IR sensors insure a high selectivity and reliability but are expensive, limiting their application. The latter measure a change in the output voltage of the sensing element caused by chemical interaction with CO₂. These are less expensive than IR, insuring at the same time good selectivity and reliability, but the working temperature is above 400 °C and the long-term response is affected by humidity.

Leal et al. [1] have studied the use of an amine surface-bonded silica gel as scrubber for CO₂ produced in industrial gaseous streams. CO₂ interacts with amine-modified silica gel forming carbamate species (scheme 1); the interaction is reversible and the adsorbed CO₂ starts to be liberated above 40 °C.



Scheme 1

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Recently a paper on CO₂ has been published by Satyapal et al. [2], investigating the stability and the long-term performance of a solid amine sorbent (known as HSC⁺ and currently used by NASA) for removing carbon dioxide in the space shuttle environment. The aim of the present work, using the same concept, is to show the possibility to chemically modify the surface of PS, obtaining an amine terminated surface, and then use it as a sensing element for carbon dioxide detection.

2 Experimental

2.1 Sample preparation PS samples were prepared by anodic etching using an ethanolic solution of hydrofluoric acid (1 : 1 HF : EtOH; v/v) starting from 48% hydrofluoric acid in water. The starting material was a p-type silicon wafer (100) oriented with a resistivity less than 1 mΩ cm. The polished silicon wafers were contacted on the back side with a strip of aluminum foil and mounted in a Teflon cell; a platinum mesh electrode was used as a counter electrode in order to insure good homogeneity of the electrical field. The anodization of PS was performed in a galvanostatic regime, applying a current density of 20 mA/cm² for 20 minutes. After etching, the samples were rinsed with pure ethanol and dried under a nitrogen stream. The resulting PS samples have a porosity of 75% ± 5% and a thickness of 12 micron calculated using a gravimetric measurement [3].

2.2 Sample modification The freshly etch samples were modified in two steps: (a) oxidation; (b) chemical modification.

a) The PS samples were exposed to a flow of ozone for 20 minutes in order to obtain a hydroxyl terminated surface; the ozone was generated with an ozone generator (OZO 2HD from Ozomax Ltd.) with a flow rate of 5 g/h.

b) The oxidized PS was placed in a 250 ml flask and 7 ml of pure 3-amino-1-propanol was added; the flask was heated at 165 °C for 3 h flowing nitrogen; after the thermal treatment the PS samples were rinsed thoroughly with ethanol and dried under a nitrogen stream.

2.3 FTIR spectroscopy The FTIR spectra were collected with a Nicolet model 550 Magna Series II Fourier Transform Infrared instrument operating in the diffuse reflectance mode, allowing *in situ* thermal treatments and gas dosages. The spectral resolution was 4 cm⁻¹ and 64 interferograms were collected for each spectrum.

2.4 Interferometric reflectance spectra The reflectance spectra were performed using an Ocean Optics CCD S 2000 spectrometer fitted with a bifurcated fiber optic probe. A tungsten lamp was used as source and the light coming from the source as well as the reflected light were collected at the surface normal. The CCD detector allows recording of spectra in the wavelength range 400–1000 nm. The PS samples were located in a flow cell using nitrogen as a carrier gas and a flowmeter to control the concentration of CO₂.

3 Results and discussions The spectra, collected in diffuse reflectance mode, of PS as synthesized, after ozone treatment and after amine modification are shown in Fig. 1.

Spectrum 1, related to the as prepared sample, shows the well-known IR absorption bands due to the presence of surface SiH_x species [4]. The ozone treatment (Fig. 1 spectrum 2) causes the appearance of terminal hydroxyl groups (Si–OH): the IR band at 3747 cm⁻¹ and the broad absorption centred at 3600 cm⁻¹ are due to stretching mode of free SiOH and hydrogen-bonded SiOH groups, respectively. The envelope of bands in the range 1250 cm⁻¹–1000 cm⁻¹ is due to stretching modes of SiO_x species.

Comparison between spectrum 3, taken after reaction with 3-amino-1-propanol, and spectrum 2 shows that the bands assigned to hydroxyl groups disappear and new absorptions are present at 3370 cm⁻¹ and 3300 cm⁻¹ (a–s stretching NH), 2940 cm⁻¹ and 2880 cm⁻¹ (a–s stretching CH of –CH₂– species) and 1600 cm⁻¹ (bending NH). This is evidence that the surface has been successfully modified. The disappearance of the 3747 cm⁻¹ band suggests an anchoring mechanism involving reaction between SiOH species and the alcoholic group of the reactant [1] (scheme 2A). The changes of the band envelope below

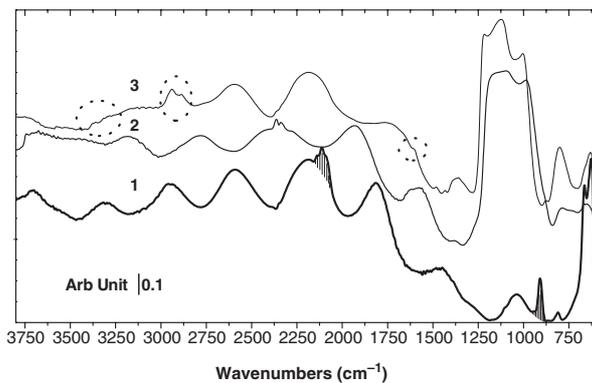


Fig. 1 FTIR spectra: 1) PS as prepared; 2) oxidized PS; 3) amine modified PS

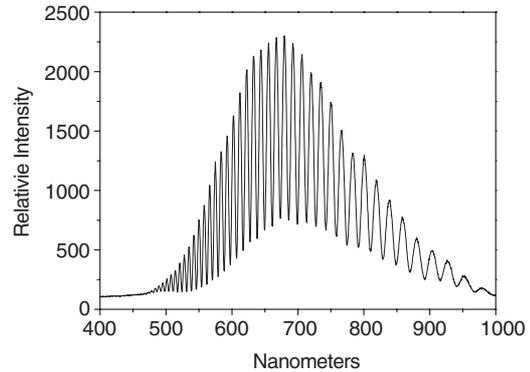
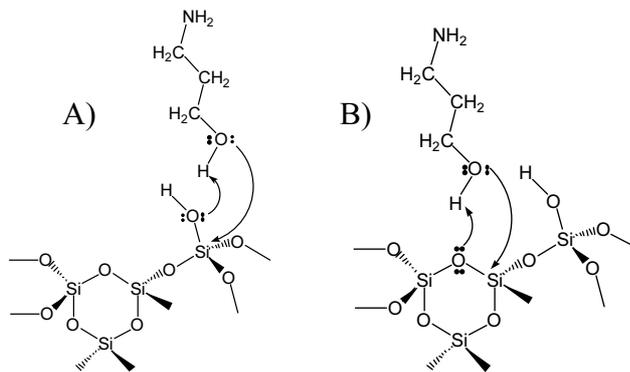


Fig. 2 Interference reflectance spectrum of PS

1250 cm^{-1} assigned to the SiO_x stretching mode suggest an alternative reaction path [5] involving the opening of Si-O-Si bonds (scheme 2B).



Scheme 2

The PS layer is smooth enough to produce a Fabry–Perot fringe pattern; the interference reflectance spectrum [6] (Fig. 2), created by multiple reflections on the air-PS interface and the bulk-PS interface, is described by:

$$EOT \equiv 2nd = m\lambda$$

where EOT is the Effective Optical Thickness, n the refractive index, d the sample thickness and m the fringe order.

The detection modality is based on the measurements of the wavelength shift of the fringe pattern shift upon adsorption of CO_2 . The interaction between the amine-modified PS surface and CO_2 causes a change in the refractive index of the medium, resulting in a shift of the fringe pattern as a function of CO_2 pressure. The same experiment was performed on an oxidized PS sample before the chemical modification: no shift was observed upon dosing with CO_2 .

In Fig. 3 the shift of the interference pattern has been reported as a function of time for different CO_2 concentrations. Before dosing with CO_2 ($t = 0$ seconds) the sample was held under N_2 flow until no shift, due to residual water impurities, was observed. The concentration of CO_2 was then increased in a step-wise fashion. The reflectivity signal was allowed to stabilize before the concentration of CO_2 was changed further. Low concentrations of CO_2 (5 to 11 parts per thousands) cause a red shift of the fringe

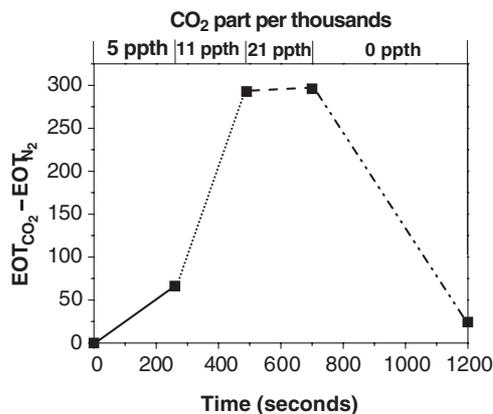


Fig. 3 Shift of the fringe pattern increasing CO₂ pressure (carrier gas: dry N₂): 5 ppt CO₂ (solid line); 11 ppt CO₂ (dot line); 21 ppt CO₂ (dash line); 0 ppt CO₂ (dash-dot line). The square points represent the maximum shift (plateau) for each pressure.

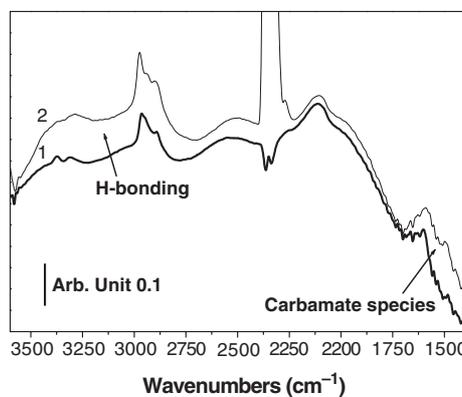


Fig. 4 FTIR spectra: 1) Amine modified PS flowing N₂ (50 cc/m), 2) amine modified PS flowing N₂ (50 cc/m) and CO₂ (5cc/m)

pattern, which saturates when the CO₂ pressure reaches 21 ppt. The red shift is presumably due to an increase of the refractive index caused by the formation of new species as a consequence of the interaction between PS-NH₂ and CO₂. The saturation behavior observed at the highest amount of added CO₂ is assigned to a saturation of the accessible amine groups. The initial spectral fringe pattern is recovered upon removal of CO₂ from the carrier gas (dash-dot line on Fig. 3), displaying the reversibility of the interaction.

The interaction of PS-NH₂/CO₂ was also investigated with FTIR spectroscopy operating in diffuse reflectance mode. The instrument set-up was similar to the experimental conditions chosen for the interference reflectance measurements. Nitrogen was used as carrier gas and CO₂ was dosed in the N₂ flow. The analysis of the FTIR data, in Fig. 4, indicates an interaction between the amine-terminated porous Si surface and CO₂: a strong OH band appears below 3600 cm⁻¹ and new bands grow in the region 1650 cm⁻¹–1300 cm⁻¹ (spectrum 2). The strong absorption centered at 2349 cm⁻¹ is due to the presence of CO₂ in the gas phase. The absorptions below 1650 cm⁻¹ are tentatively assigned to an ammonium carbamate species based on comparison with literature values [7]. The reaction involving the amines and CO₂ is reversible: the spectrum 1 is completely recovered when CO₂ is removed from the carrier gas.

4 Conclusions Treatment of porous Si with a hydroxylamine produces a material with an FTIR spectrum consistent with an amine-terminated surface. The surface species generated in this reaction then reacts reversibly with CO₂ to produce changes that are observable in both the visible and infrared spectra of the porous Si films. Although the chemical nature of the surface species both before and after binding of CO₂ is not clear at this time, a carbamate species is suggested. The work demonstrates that CO₂ can be reversibly sensed with this material. The detection limit shown in this work is still far from the market requirements, but the reversibility and low cost of this system represents a starting point for future development and an alternative to non-dispersive IR and electrochemical sensors.

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