Fabrication and characterization of zeolitic imidazolate framework-90 (ZIF-90) absorbers for carbon dioxide sensing at near infrared band

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ABSTRACT

In this work, layers of crystalline zeolites formed by tetrahedrally-coordinated Zn ions bridged by imidazolate (ZIF-90) were deposited in order to investigate the desorption and absorption of CO_2 and apply these layers as pre-concentrators for CO_2 detection. For the deposition of ZIF-90 layers by casting, it was proposed an alternative chemical solution which employs ethanol as solvent instead of methanol, as reported in the literature, to provide a less toxic process to humans and allows one applications of CO_2 storage. Several layers were deposited using a solution prepared from a mixture of zinc nitrate (4.3g) and 2-methylimidazole (9.7g) with several dilutions in ethanol to vary the pH in the range of 7.2 to 8.2. As a result, repetitive layers of approximately 7.5μm in thickness were deposited on the silicon wafers by casting. After annealing these layers at a temperature of 150 °C for 48h in ultra-pure nitrogen, nanocrystals with size distributions in the range of 5 to 400nm with a ZIF-90 crystal structure were achieved only for pH next to 7.2. From infrared (IR) measurements of the ZIF-90 layers, it was observed a band located at 2337cm^{-1} that increases with the increase of the CO_2 pressure and with the exposure time to this pressure. In addition to the band at 2337cm^{-1}, it was observed a second band at 2360 cm^{-1} indicating two different responses: (i) the band at 2337cm^{-1} is related to a substantial quantity of the CO_2 molecules absorbed into the layer along the contours of the nanocrystals or within the crystal structure and (ii) the band at 2360cm^{-1} is related to the portion of CO_2 molecules adsorbed on the surface. Also, if the ZIF-90 layer is exposed to CO_2 at atmospheric pressure for at least 2h, a 10ppm sensitivity to CO_2 is achieved considering the minimum absorbance as being 0.001 and the loading time at the atmospheric pressure as at least 20min.

Index Terms: ZIF, crystalline zeolites, Zn-Im-Zn chains, ZIF-90, CO_2 absorption, CO_2 detection.

I. INTRODUCTION

The first mineral zeolite, the stilbite, was discovered by the Baron A. F. Cronstedt in 1756 [1]. But, it was only in 1926 that their adsorption characteristics were attributed to the small pores of about 0.5nm in diameter in order to explain the permeation of small gas molecules. For this reason, the term "molecular sieve" was proposed [2]. Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), are microporous crystalline materials with tetrahedral networks [3,4]. Compared to other MOFs, ZIFs exhibit excellent thermal and chemical stability due to the strong bonds between the imidazolate anions and metal cations [3].

ZIF-90 is one of the most studied ZIF structures, and it has a sodalite structure with pore aperture of 0.35 nm, which is larger than the kinetic diameter of H_2 (0.289 nm), and CO_2 (0.33 nm), and smaller than N_2 (0.364 nm) and CH_4 (0.38 nm). Also, ZIF-8 have a sodalite structure but with pore aperture of 0.34nm, which means similar properties compared to ZIF-90. Due to their small pore diameter, ZIF-90 and ZIF-8 have shown great potential for industrial applications in H_2 and CO_2 adsorption and separation [4-8]. In addition, ZIF-90 and ZIF-8 have a high chemical resistance to boiling alkaline solutions and organic solvents [3,8]. Thanks to these excellent characteristics, ZIF-90 and ZIF-8 have been used for sensing oxygen, solvent molecules, metal ions, DNA, proteins and other important biomolecules [8-10].

Nowadays, nondispersive infrared (NDIR) sensors are the most common type used to measure CO_2. They are spectroscopic sensors to detect CO_2 in a gaseous environment by its characteristic absorption at a wavelength around 4.3μm (wavenumber around 2350cm^{-1}). The key components are an infrared source, a light tube, an interference filter, and an infrared detector. The gas is pumped into the light tube, and the electronics measures the absorption of the characteristic wavelength of light. The best sensitivity achieved until now is 20-100ppm [11].

In this work, it is proposed the near infrared measurement of gaseous CO_2 previously absorbed in zeolitic imidazolate framework-90 (ZIF-90). To achieve this goal, for the first time, ZIF-90 films were deposited

directly onto silicon wafers in order to be compatible with the silicon technologies for integrated circuits, to work as a pre-concentrator and increase the sensitivity to both the CO_2 pressure and the CO_2 flow. It is worth of note that the ZIF-90 was used for the first time as a pre-concentrator for detecting CO_2 by infrared and an alternative recipe for its obtention was also proposed.

II. EXPERIMENTAL PROCEDURES

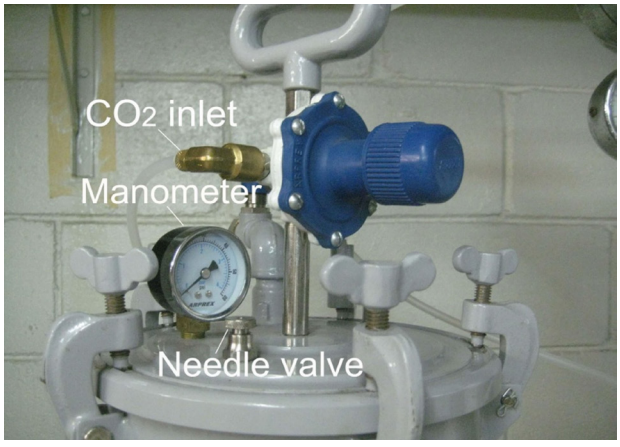
Si-p wafers (100), 3 inches in diameter, were chemically cleaned by using a conventional RCA cleay ning [12]. Zeolitic imidazolate framework-90 (ZIF-90) was synthesized as follows: 4.3 g of zinc nitrate hexahydrate ($ZnNO_3.6H_2O$) was first dissolved in 100, 400 or 800mL of ethanol; then 9.7 g of 2-methylimidazole ($C_4H_6N_2$) was subsequently dissolved in the same solution; after that the solution was stirred for 60min at room temperature. It is important to call attention that the different quantities of ethanol used, 100, 400 or 800mL, meant pH of 8.2, 7.6 and 7.2, respectively. Following, 10mL of the fresh solution was dripped and spread over the rough side of the Si wafer and it was kept drying at the room temperature during 10min. Finally, the wafers were annealed at 150°C for times ranging from 0 to 48h in ultrapure N_2. As a result, 7.5-10μm thick films were obtained on the Si-p wafers. This recipe for depositing ZIF-90 is new because it uses ethanol instead of methanol [13] and, for the first time, it was employed silicon wafers as substrates in order to be compatible with the silicon technologies for integrated circuits.

Field-emission scanning electron microscope (SEM) pictures were taken with the aid of a FEI Nano-SEm 400 FEG, with an acceleration voltage of 10kV.

X-ray diffraction (XRD) patterns were recorded at room temperature with the aid of a PIXCEL 3D Panalytical diffractometer using CuKα radiation (λ = 1.54059 Å) at 40kV and 40mA.

Infrared (IR) absorption spectra were recorded at room temperature on a Biorad FTS 6000 equipment in the range of 400 to 3000cm^{-1}. The spectra were obtained at room temperature in controlled conditions of low humidity using ultrapure nitrogen flux. To characterize the processes of absorption and adsorption of CO_2 by the deposited ZIF-90 layers, the setup shown in Fig. 1 comprises a CO_2 chamber with adjustable pressure in the range of 0 to 32psi feeded by a cylinder of ultrapure CO_2 with an outlet regulator. Fig. 1b shows details of the CO_2 inlet, the manometer used for measuring the internal pressure of the chamber and a needle valve for fine adjustment of the pressure. After conditioning the ZIF-90 samples at different pressures and exposure times in CO_2, the temporal evolution of the CO_2 bands in the IR spectra was characterized.

(a)



(b)

Figure 1. (a) Setup employed for CO_2 conditioning of the ZIF-90 samples at different pressures in the range of 0 to 32psi and different exposition times (0 to 150min); (b) Detail of the CO_2 inlet, the manometer and the needle valve for the fine adjustment of the pressure.

III. RESULTS AND DISCUSSION

As mentioned in the experimental procedures, different volumes of ethanol were tested in order to synthesize zeolitic imidazolate framework-90. Fig. 2 shows typical XRD patterns for layers prepared with 100, 400 and 800 mL of ethanol, respectively. It was observed the formation of ZIF-90 only when 800 mL of ethanol was employed. The increase of the solvent content from 100 to 800 mL makes the pH vary from 8.2 to 7.2, respectively. The pH close to 7.0 is pointed out as the main factor to be controlled in order to have a successfully formation of zeolitic imidazolate framework with high degree of crystallinity [13]. In addition, it was also observed a high stability of the pH for several hours after the preparation of the ZIF-90 deposition solution.

The best results were consistently obtained for ZIF-90 layers deposited by casting using the recipe de-

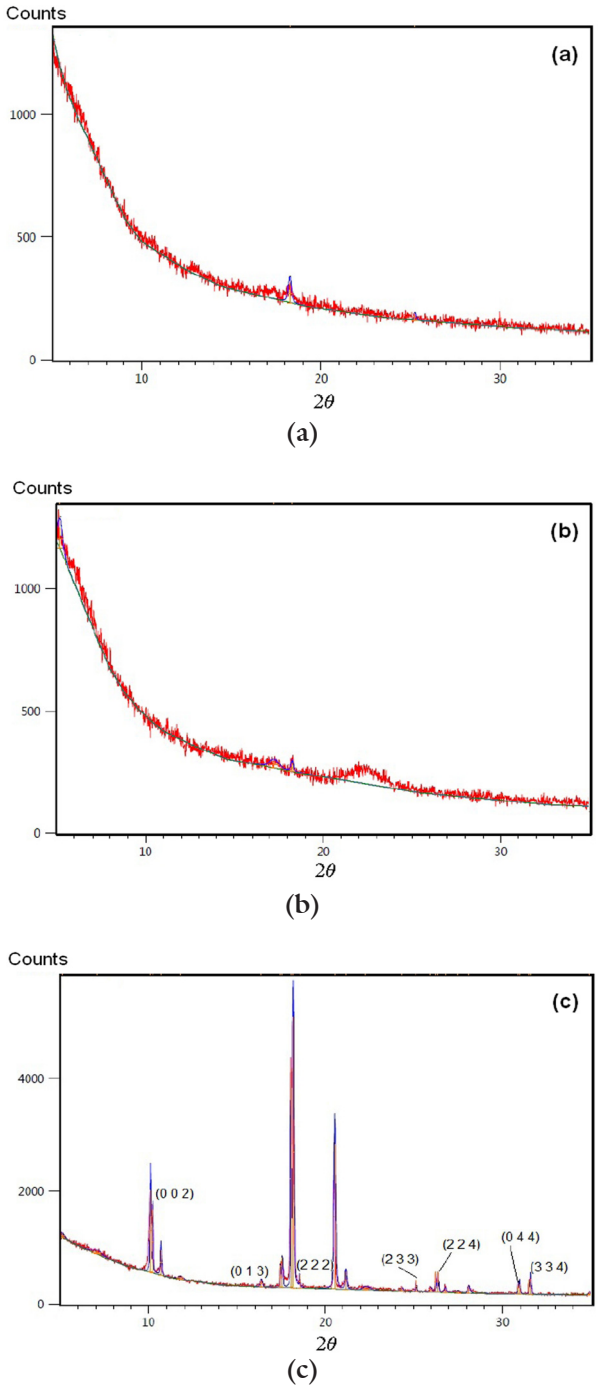


Figure 2. Typical XRD patterns for samples prepared with: (a) 100mL of ethanol, (b) 400mL of ethanol and (c) 800mL of ethanol.

scribed in the experimental procedures with pH = 7.2. In order to optimize the amount of nanocrystals for layers few micrometers thick, the heat treatment at 150°C in ultrapure nitrogen was tested for times varying from 0 to 48h. Fig. 3 illustrates the typical morphology of nanocrystals obtained for layers deposited by casting (10ml) that underwent treatment at 150°C for 48h in ultrapure nitrogen. It is important to note that the

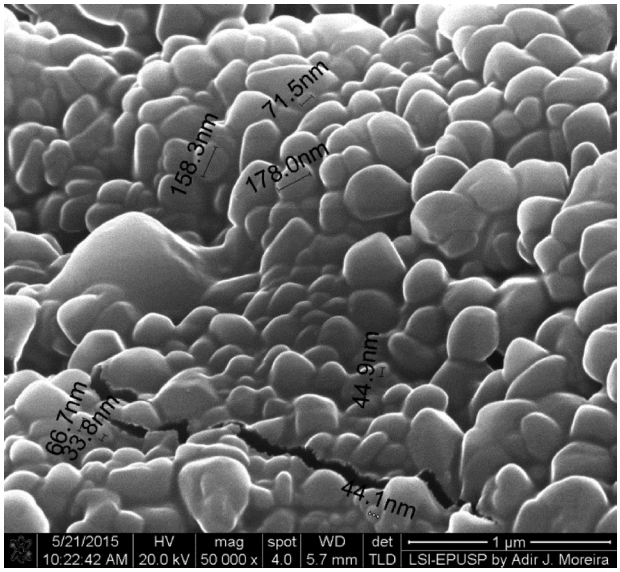


Figure 3. Typical FESEM image for ZIF-90 layers deposited by casting (50ml) annealed at 150°C for 48h in ultrapure nitrogen.

formed nanocrystals showed sizes in a wide range from 5 to 400nm. This fact indicates that a crystalline phase different of ZIF-8 was predominantly formed because the characteristic size of the ZIF-8 nanocrystals should be in the range of 5 to 10nm [13].

The crystalline phases of the nanocrystals ZIF-90 shown in Fig. 3 were obtained from the XRD spectrum shown in Fig. 2c. It is important to call attention again that the ZIF-90 formation was observed only when the chemical solution was diluted in 800ml of ethanol. The pH of 7.2 was the main factor to be controlled in order to successfully deposit ZIF-90 layers. Furthermore, it was also observed a high stability of the pH for several hours after preparation of the chemical solution.

After an exhaustive search in the literature, only the XRD pattern of the ZIF-90 structure was compatible with all the crystal facets observed in the XRD spectrum of the Fig. 2c. It was employed two decimal places for fitting all the angles in the XRD pattern (7.50°, 10.26°, 11;77°, 15.39°, 16.42°; 17.52°, 19.94°, 20.54°, 21.19°, 22.28°, 24.31°, 25.11°, 26.16°, 28.08°, 30.34°, 31.53°) [14].

Fig. 4 shows typical FTIR spectra for ZIF-90/Si-p after different conditioning in CO_2 at different pressures and for different times. At first, the IR spectrum of the reference ZIF-90 (Fig.4a) is consistent with that previously reported in the literature [8, 14-16], concerning to the ranges of 700 to 2300cm^{-1} and above 2500cm^{-1}. At second, the two strong absorption bands at ~670 and ~2337cm^{-1} in the ZIF-90 spectrum are attributed to the bending mode (v2) and asymmetric stretching mode (v3) of the C=O bonds, respectively. It is worth of note in Fig. 4 that the signal

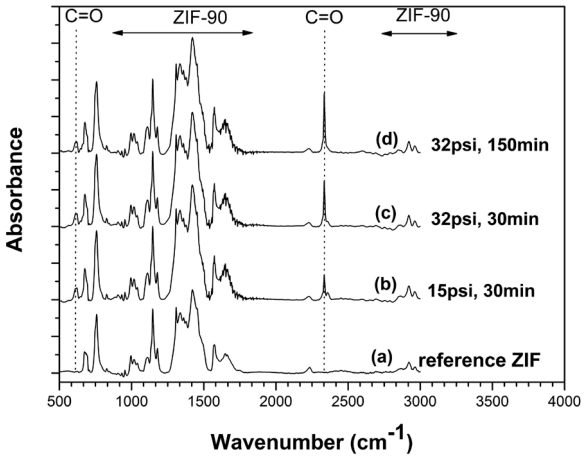


Figure 4. Typical FTIR spectra for ZIF-90/Si-p after different conditioning in CO_2: (a) reference ZIF-90 without conditioning, (b) 15psi for 30min, (c) 32psi for 30min and (d) 32psi for 150min.

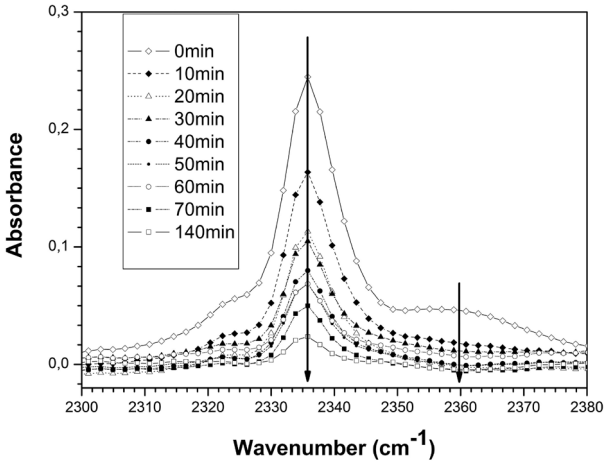


Figure 5. Typical FTIR spectra for ZIF-90/Si-p, as function of the time, after conditioning in CO_2 at 32psi during 90min.

of the asymmetric stretching mode increases with the increase of the CO_2 pressure and with the time interval in which the pressure is kept. As it will be shown in the following, the increase of this signal is due to the storage of CO_2 in the ZIF-90, which works as an adsorber.

Fig. 4 shows two components at 2337cm^{-1} and 2360cm^{-1}, here called as doublet, which indicates two different mechanisms of CO_2 adsorption. By analyzing the peak heights and their evolution toward the recovering to the ZIF-90 reference spectrum, the component at 2337cm^{-1} can be interpreted as a substantial portion of CO_2 molecules inserted into the ZIF-90 film at the contours of the nanocrystals or inside of the framework and the component at 2360cm^{-1} can be interpreted as a portion of CO_2 molecules adsorbed on the surface of the ZIF-90 film, which may be easily desorbed. These facts will be highlighted in the following.

Fig. 5 shows the evolution of the peak height at 2337 cm^{-1} as function of the time after conditioning the ZIF-90 film in CO_2 at 32 psi during 90 min followed by immersion in ultrapure N_2 (5 L/min). With the cessation of the CO_2 loading, the peak height progressively decreases. In addition, fig. 6 shows an exponential decrease of the peak height with the time that is consistent with a dominant diffusion process from the film to the N_2 environment as predicted by the equation of mass conservation [17]. On the other hand, the evolution of the peak height at 2360 cm^{-1} is too fast, which corroborates a rapid desorption of the adsorbed portion of CO_2 molecules from the surface of the ZIF-90 film as mentioned before.

Figure 7 shows the evolution of the peak height at 2337cm^{-1} and and 2360cm^{-1}, respectively, as

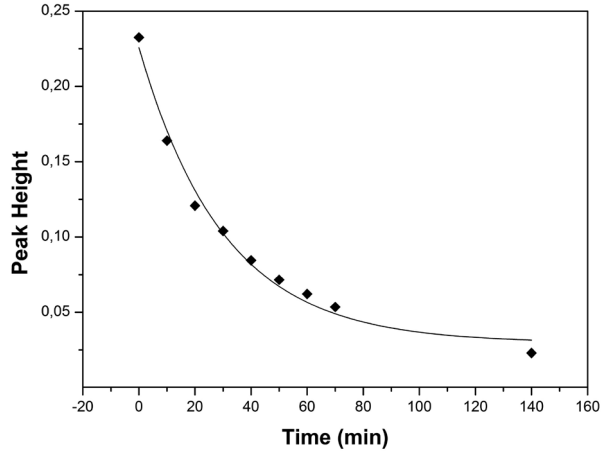


Figure 6. Peak height at 2337cm^{-1} as function of the time after conditioning the ZIF-90 film in CO_2 at 32psi during 90min followed by immersion in ultrapure N_2 (5L/min).

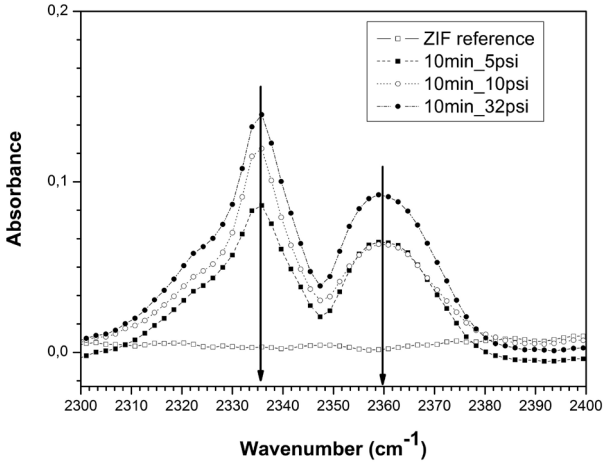


Figure 7. Typical FTIR spectra for ZIF-90/Si-p, as function of the CO_2 conditioning pressure during 10min. The FTIR spectra were extracted immediately after the CO_2 conditioning.

a function of the CO_2 conditioning pressure during 10min followed by immediate extraction of the IR spectrum of the sample inserted in ultrapure N_2 atmosphere (5L/min). It is important to note that the height of the peak at 2337cm^{-1} corresponding to the absorption of CO_2 diminishes 14.3% when the pressure decreases from 32 to 10 psi and diminishes 38.6% when the pressure decreases from 10 to 5 psi. Also, the peak at 2360 cm^{-1} diminishes 32.6% when the pressure passes from 32 to 10 psi and no variation to go from 10 to 5psi. These facts observed for peaks at 2337cm^{-1} and 2360cm^{-1} allow to conclude, respectively: (i) the higher the conditioning pressure, the more difficult it becomes the diffusion out of the body of the film (see 2337cm^{-1}) and (ii) the easier is the desorption from the surface layer (see 2360cm^{-1}). These facts are also consistent with the diffusion processes from the body out of the layer as well as the desorption from the surface layer as reported in literature [17].

Figure 8 shows the evolution of the peak height at 2337cm^{-1} and at 2360cm^{-1}, respectively, as a function of the conditioning time in CO_2 at a pressure of 32psi followed by immediate extraction of the IR spectrum under ultrapure nitrogen flux (5l/min). It is important to note that the height of the peak at 2337cm^{-1} corresponding to the absorption of CO_2 enhances substantially when the conditioning time is 150min (absorbance 0.3) and diminishes 25.6% when the conditioning time decreases from 150 to 90min. and also diminishes more 42.6% when the conditioning time decreases from 90 to 10min. Moreover, the peak at 2360 cm^{-1} shows a great increase of 49.5% when the conditioning time decreases from 150 to 90min and more 40.3% when the conditioning time decreases from 90 to 10min. This means that the higher content of CO_2 molecules inside the film is capable of pushing a higher quantity of CO_2 molecules adsorbed on the surface, that is, a higher desorption of the surface molecules. These facts observed for peaks at 2337cm^{-1} and 2360 cm^{-1} allow to conclude, respectively: (i) the longer the conditioning time at the pressure of 32psi, the more difficult is the diffusion out of the body of the layer and, (ii) the longer the conditioning time at the pressure of 32psi, the easier is the desorption of the CO_2 molecules from the surface pushed by the CO_2 molecules that are coming out of the ZIF-90 film. These facts are also corroborated by the literature [17].

Fig. 9 illustrates the typical FTIR spectra as function of the time after film conditioning in a CO_2 flow of 0.5L/min on the ZIF-90 surface during 10min at the atmospheric pressure. It is worthy of not that after the cessation of the CO_2 flux, the peak height at 2337 cm^{-1} progressively decreases and the the evolution of the peak height at 2360 cm^{-1} is faster although the initial heights of the doublet are almost the same. Again, this fact corroborates a rapid desorption of the adsorbed portion of CO_2 molecules from the surface of the ZIF-90 film. In addition, based on the results until now, ZIF-90 is an excellent pre-concentrator for CO_2 gas whose CO_2 loading increases with the gas pressure and with the time of loading. In addition, it was observed a sensitivity of 10ppm for CO_2 if the loading time at the atmospheric pressure is at least 20min in order to achieve a measurable absorbance inferior limit of 0.001.

IV. CONCLUSION

In conclusion, it was presented the fabrication and characterization of zeolitic imidazolate framework 90 (ZIF-90) absorbers for sensing CO_2 at near infrared band. ZIF-90 films were deposited directly onto

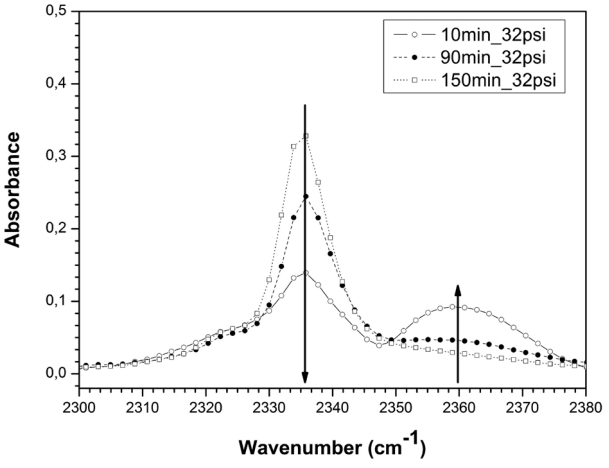


Figure 8. Typical FTIR spectra for ZIF-90/Si-p, as function of the conditioning time in CO_2 at 32psi.

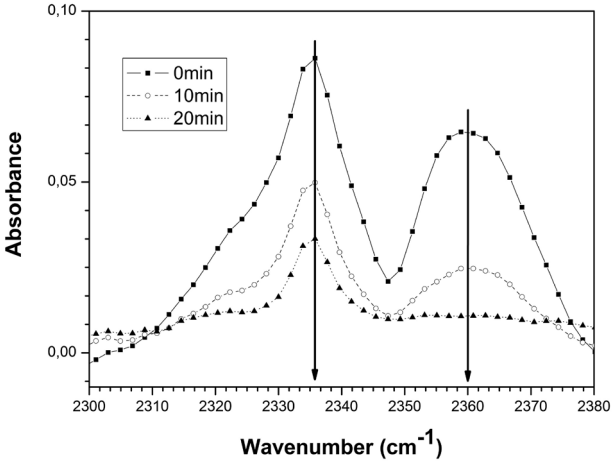


Figure 9. Typical FTIR spectra for ZIF-90/Si-p, as function of the time, after conditioning in CO_2 flux of 0.5L/min on the ZIF-90 surface during 10min.

silicon wafers in order to be compatible with the silicon technologies for integrated circuits, to work as a pre-concentrator and increase the sensitivity to both the CO_2 pressure and the CO_2 flow. In addition, an alternative recipe for ZIF-90 obtention was also proposed.

For CO_2 detection using near infrared absorption, it was worthy of note that the signal of the asymmetric stretching mode at 2337 cm^{-1} increases with the increase of the CO_2 pressure and with the time interval in which the pressure is kept. Besides the component at 2337 cm^{-1}, a second component was also observed at 2360 cm^{-1}, indicating two different mechanisms of CO_2 adsorption. By comparing the height and the evolution toward the recovering to the ZIF-90 reference spectrum, the component at 2337 cm^{-1} was interpreted as a substantial quantity of CO_2 molecules inserted into the ZIF-90 film at the contours of the nanocrystals or inside of the framework and, the component at 2360 cm^{-1} was understood as a portion of CO_2 molecules directly adsorbed on the surface of the ZIF-90 film.

Finally, it was observed a sensitivity of 10ppm for CO_2 if the ZIF-90 loading time at the atmospheric pressure is at least 20min in order to achieve a measurable absorbance inferior limit of 0.001. This result corroborates the use of ZIF-90 as pre-concentrator since it improves the detection limit for CO_2 [11].

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