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ORIGINAL ARTICLE

Optical and morphological characterization of bispyrazole thin films for gas sensing applications

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Abstract The optical gas recognition capabilities of thin film layer of 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol deposed on quartz substrates were studied. The dynamic gas responses to the following analytes have been investigated as air pollutants (SO_2, NO_2, CO, CH_4 and NH_3). The spin-coated bispyrazole layer appears to have reversible response towards SO_2 and a very low and irreversible response to NO_2. The selectivity of the thin film based on bispyrazole layer with respect to other analytes was also examined and the present data show that the thin sensing layer in the presence of CO, CH_4 and NH_3 in low concentration does not influence its optical properties.

1. Introduction

Gas detection devices are increasingly needed for health of the people working in industries, safety, environmental monitoring, and process control (Gubillas et al., 2009; Beche, 2010; Seker et al., 2000). To meet this demand, considerable research into new sensors is underway, including efforts to enhance the performance of traditional devices, such as resistive metal oxide sensors through nanoengineering. As an alternative, there has been great interest in trying to exploit the properties of organic materials. These materials offer a number of advantages over inorganic sensors. Firstly, there is an enormous range and diversity of organic semiconducting devices when compared with the available options amongst inorganic ones. There is an increasing technological interest in the synthesis of organic nonmaterial in the perspective of fabrication of devices showing specific molecular properties. A further factor of importance is the inherently small size of the molecular subunit, offering the possibility of considerable size reductions in devices. Amorphous organic thin films with high charge carrier (hole or electron) mobility have found wide applications in

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optoelectronic devices, such as organic solar cells (Miller et al., 1991), dye-sensitized nanocrystalline semiconductor solar cells (Bach et al., 1998; Xu et al., 2009), and organic light-emitting diodes (OLEDs). Particularly, pyrazole-based thin films have been applied in OLEDs as whole transporting materials due to their good hole-transporting and film-forming abilities (Wu et al., 2000). Different examples can be found in the literature about the use of pyrazole-based ligands in the preparation of new ion selective membrane sensors for transition metal ions and various anions (Kumar et al., 2008), in ion-selective membrane sensors. A convenient method for fast analysis with high sensitivity and selectivity still unexplored for this kind of molecules is gas sensing for environment monitoring. For this purpose, the appeal of reversible gas detection at low concentration levels has become fundamental in the perspective of fabrication of highly sensitive gas sensors; proper devices with rapid and accurate sensing are greatly requested (Massari et al., 2003). Numerous efforts have been directed to developing SO_2 or NO_2 gas sensors, by mainly employing solid electrolytes, such as alkali metal sulfates (Imanaka et al., 1987), Ag-β-alumina (Yang et al., 1996), Na-β-alumina (Akila and Jacob 1989). NASICON ($Na_2Zr_2Si_3PO_{12}$) (Choi et al., 1996), and MgO stabilized ZrO_2 (Yan et al., 1994), the latter three materials have been combined with an appropriate auxiliary phase. Other contributions have been directed to the realization of chemiresistor sensors based on the use of metal-oxides or organic sensing material (Brunet et al., 2008). In this work, we report a first attempt to use bispyrazole-based material as sensing layers in chemical gas sensors, which is based on a change of optical UV–Vis absorption curves. Simple optical methods to detect gases are based on the measurement of some physical variation properties of the active layer induced from the absorption of the gas molecules on its surface. There are many optical methods that can be applied to monitor the flue gas emission, such as chemiluminescence, laser induced fluorescence (LIF) and differential optical absorption spectroscopy (DOAS) (Guanghua et al., 2009). In this work, a 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol (Bouabdallah et al., 2007) (Fig. 1) is used in thin film form as sensing material for pollutant gas detection. The encouraging results that the investigated material showed an interesting response towards SO_2 gas demonstrate that it is suitable for optical gas-sensor. In addition, sensor responses to NO_2, CO, CH_4 and NH_3 in low concentration were also tested.

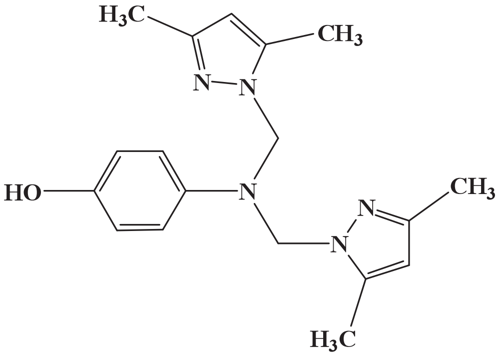

Figure 1 Schematic drawing of 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol.

2. Experimental

2.1. Reagents

All reagents and solvents were purchased from Aldrich Chemical Co. The gases utilized for optical characterization were obtained from Rivoira.

2.2. Thin films deposition

All the sensing layers were prepared in thin film forms by spin coating (Fig. 2) using a prepared solution on suitably cleaned quartz substrates. Fused silica substrates (4 mm × 18 mm, 1 mm thick) were cleaned by immersion in boiled acetone for 5 min and then in boiled isopropyl alcohol for 5 min and left to cool at room temperature under N_2 purge. Then, the spin-coated thin films were prepared using chloroform as a solvent, and by spinning the solution at 2000 rpm for 30 s onto the quartz substrates. Different thickness of the thin films was obtained by varying concentrations of the starting solution and spinning rate of the substrate.

2.3. Optical measurements in controlled atmosphere

Absorption spectra of a solution containing 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol and of spin-coated thin films deposited onto quartz substrates were measured by using a Cary 100 Scan UV–Vis spectrophotometer. The surface topography of the film was investigated by contact mode atomic force microscopy (AFM) using a

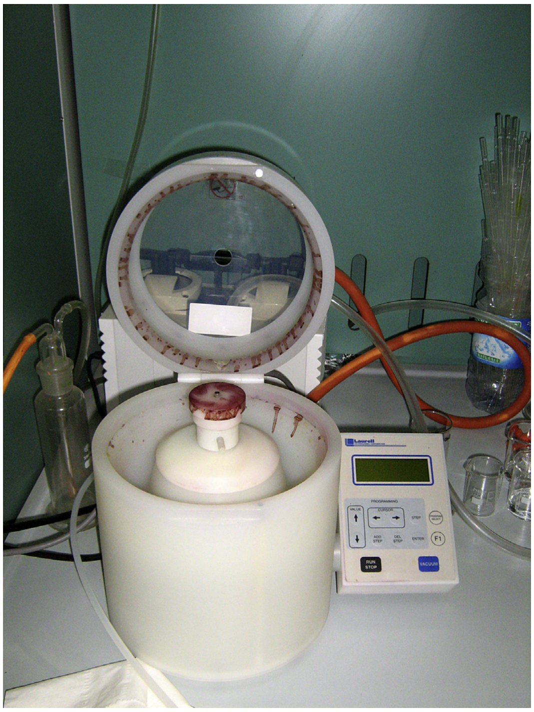

Figure 2 Photo of experimental apparatus used for spin coating.

VEECO EXPLORER system equipped with a Si_3N_4 pyramidal tip by using a low cantilever's force applied to the surface. The same AFM equipment was used to measure the thickness of the films by doing a simple scratch onto the surface. All the optical measurements in the UV–Vis spectral range were performed in controlled atmosphere, at room temperature and at normal incidence of the light beam by using a filtered light source from AVANTES tungsten–halogen lamp guided into an optical fiber and the absorption spectra were registered and analysed using a multichannel commercial spectrophotometer AVANTES mod MC 2000 (Fig. 3). The spectrum A_0 of the thin active layer was first measured in dry-air flow and used as the standard reference for measuring the spectrum A of the film in the presence of gas. The absorption properties of the active layer were measured in a dynamic pressure system implemented in our laboratory where dry air at ambient pressure was used as carrier and reference gas, as elsewhere reported (Spadavecchia et al., 2006). The gas mixing station consists of a mass flow controller MKS Instruments model 647B equipped with two mass flow meters/controller and a system of stainless steel pipelines and switching valves. The samples were put in an independent stainless steel test chamber; all placed in the principal tube of the test bench in a series using Swagelok connections into suitable slots for sensors to expose all the thin films to the same gas concentration under the same experimental conditions. The experimental procedure was started by the flowing of dry air through the sample chamber until a steady absorbance reading was obtained. Then, samples were exposed to a flow of gas until a saturation signal was obtained, which allowed us to calculate the response of the sensor. The active gas was then turned off and the sample was left to recover in air. At this point, a higher concentration of the active gas was admitted to the chamber and the measurement procedure was repeated. The output flow rate used throughout these studies was 100 sccm according to the dimension of the test chamber.

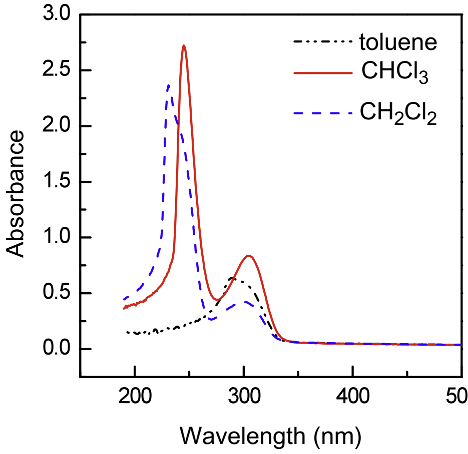

Figure 4 UV–Vis spectrum of 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol dissolved in various solvents

3. Results and discussion

3.1. Optical characterization of solution

Before the deposition process, optical absorption spectra in the UV–Vis spectrum range of the starting solution containing 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol were recorded. Fig. 4 shows the UV–Vis spectra of the sample in three different solvents. The UV–Vis spectrum of the sample prepared in dichloromethane is characterized by two absorption bands centered at 300 and 234 nm. In chloroform, as well, two main bands centered at 244 and 305 nm are evident. It is to note that the UV–Vis spectrum in toluene solution is characterized just by one absorption band centered at about 290 nm. These spectral differences were due to the difference of solvent polarities.

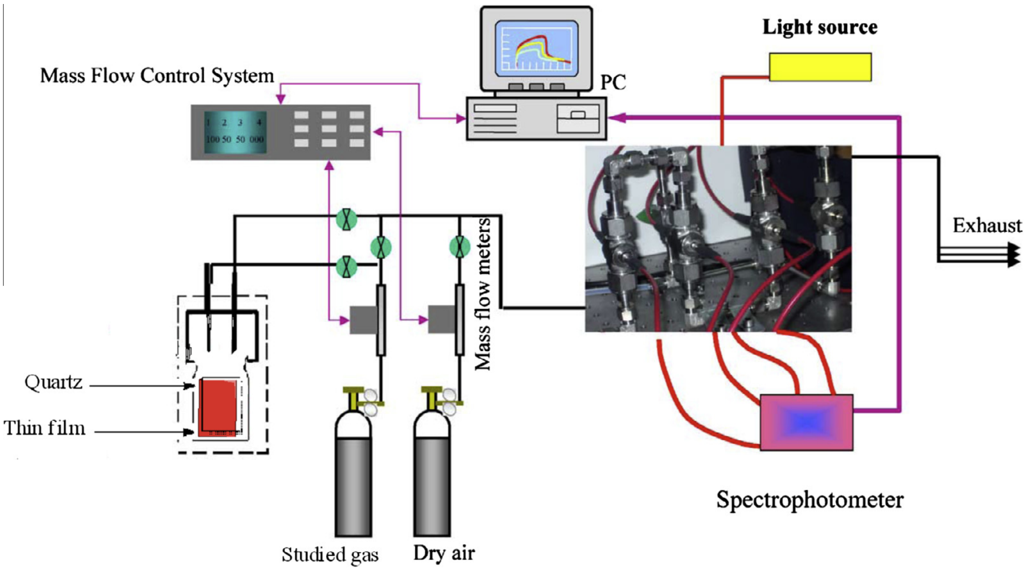

Figure 3 Scheme of the experimental apparatus used for optical tests in controlled. Atmosphere

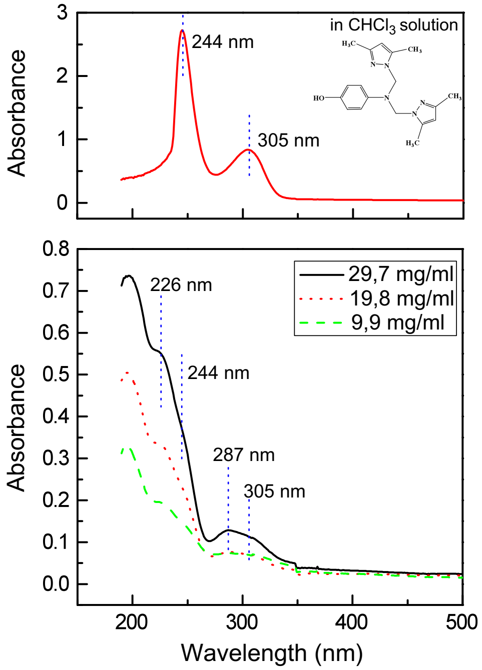

Figure 5 UV–Vis spectrum of 4-[bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino]phenol thin films spin coated on quartz substrate at 9.9, 19.8 and 29.7 mg/mL concentration of the analysed material in chloroform solution, respectively. A spectrum of the same compound in solution is reported for comparison.

3.2. Optical characterization of thin solid films

The deposited films, obtained at different concentration of the starting solution, were optically characterized by UV–Vis. Fig. 5 shows the optical absorption of the deposited thin film starting from a chloroform solution with concentrations of 9.9, 19.8 and 29.7 mg/mL, respectively. All the absorption curves are characterized by absorption bands centered at about 244 and 305 nm. The blue shift of the absorption bands at about at 226 and 287 nm can be due to the formation of complexes during the formation of thin film by spin coating.

This distribution of aggregates can have many advantages, such as the formation of homogeneous nanometer pores, deep porous layer, distributed on a quartz surface. The final thickness of the analysed sensing layer is within 100 nm. Moreover its striking simplicity, shorter fabrication time, higher uniformity, better reproducibility and most importantly the longer durability of the sensing layer in air or in aqueous media are the greatest advantages of this material as a potential candidate in biomedical applications (Spadavecchia et al., 2006; Li et al., 2010; Sigoli et al., 2008).

Generally, the typical absorption peaks of these molecules in solution are due to the electron transition π–π^* of the singles molecules. During the formation of the thin films, we usually observe binary or tertiary molecule complexes. This aggregation is responsible for the blue shift in the absorption bands registered in solution.

3.3. Morphological characterization by AFM

In order to check the lateral uniformity of the thin films, images were taken from various areas of the sample surface, and at different scan sizes. The images were analysed and processed using the standard software supplied with the control electronics. Fig. 6 shows a 20 μm × 20 μm image of the thin film obtained form a starting chloroform solution having a concentration of 29.7 mg/mL. It corresponds to the sample showing the best sensor performances. AFM characterization indicates, a smooth surface with different aggregates randomly distributed on the surface, whose size distribution is inhomogeneous over the whole film surface ranging between 20 nm and few μm. The above aggregates are supposed to be originated by the assembly of a great number of molecules. These structures increase the roughness value measured and, also the experimental error associated, showing the wide range of values that can be measured all over the sample. This effect was more evident as the scan range increases.

3.4. Optical sensing properties

The optical responses of the thin film in the presence of different gases (i.e. SO_2, NO_2, NH_3, CO and CH_4) were measured by allowing the flow of each gas into the pipeline of the

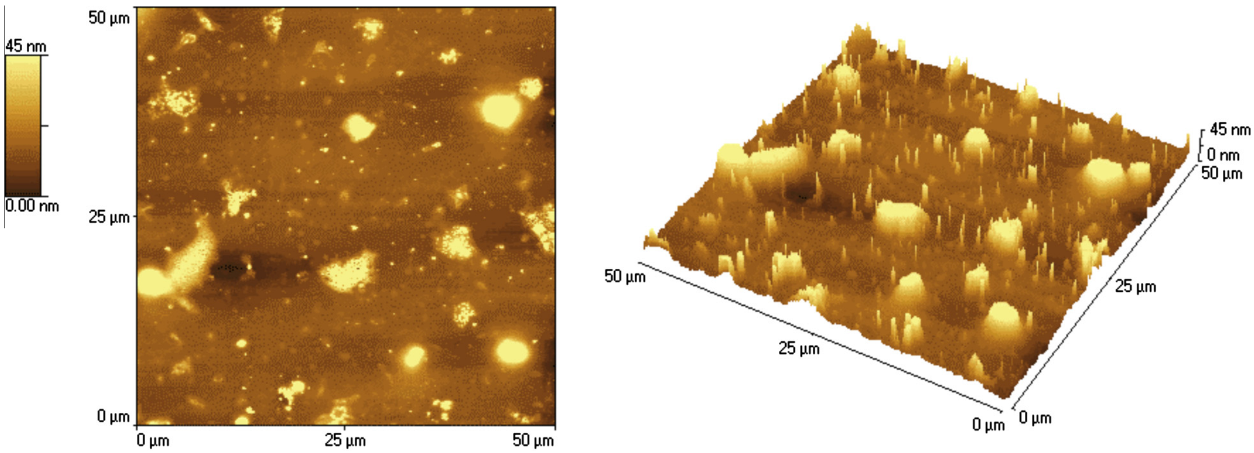

Figure 6 20 μm × 20 μm AFM image in 2 and 3 dimensions of the bispyrazol-based thin film obtained by spin coating the starting chloroform solution (29.7 mg/mLl) onto quartz substrate before gas sensing tests.

experimental apparatus. Optical detection methods, which are based on absorption or emission spectroscopy offers enhanced sensitivity and good selectivity in gas detection. Our approaches have two great advantages: Firstly, by directly probing the petrochemical changes of the species, when the interrogating wave length coincides with the absorption band of the analyte. Secondly by utilizing an analyte specific reagent to transduce the analyte concentration into an optical signal (Mechery and Singh, 2006; Cleary et al., 2002).

The dynamic response was measured by recording the integral area (A) of the absorption spectrum in the selected wavelength region versus time on independent channels. We fixed 5 min as the period of exposure to the gases, and 5 min as recovering period in dry air. The analysed sensing layer was obtained by using a concentration of 29.7 mg/mL in chloroform. Fig. 7 shows the response of the thin film in the presence of dry air, and a mixture containing 500 and 1000 ppm SO_2 in dry air. An interesting but small variation in the sensor signal was observed when the sensing layer was exposed to a mixture containing SO_2 gas. In particular the variation rises upon increasing the gas concentration from 500 ppm ($\Delta A = 228$) to 1000 ppm in dry air ($\Delta A = 457$). The evidence of these variations was confirmed by the comparison of the responses ΔA calculated as a difference ($A_{\text{gas}} - A_{\text{dry-air}}$), where A_{gas} is the integral area under the absorption peak corresponding to the wavelength region between $\Delta\lambda = 220 \div 400$ nm measured in the presence of the gases and $A_{\text{dry air}}$ is the same integral area measured in dry air flux in the same wavelength range. This signal was proportional to the number of absorption sites available to the interaction between the gas molecules and the sensing layer. Pyrazol is generally an electron donor material, so any interaction mechanism between analysed gas molecules and sensing material can be influenced by this characteristic, which can be improved by a suitable coordination with other transition metals, such as copper, cobalt or zinc. As shown in Fig. 8 it is possible to observe the response of the thin film in the presence of dry air and SO_2 at the highest concentration; the restoring at the initial value of the absorbance spectrum confirms the reversibility of the interaction during the cycles of the measurement. The coordination behaviour of bispyrazole ligands with transition metals is well known. They can coordinate these metals via their two sp^2 and sp^3 nitrogen units (Scarpellini et al., 2005; Gatjens et al., 2009; Sheu et al., 1995; De Oliveira et al., 2008; Banerjee et al., 2010). Our ligand acts as an acceptor in n-type semiconductor, which results in a band bending in the appearance of a depletion region near the surface. Detection of other species including NO_2 is realized through their reaction with the nitrogen atoms causing increase or decrease of band bending (Tsiulynu et al., 2007; Sessler et al., 2006). In Fig. 9, the response of the thin film to the presence of dry air and NO_2 is also reported. However, the signal was unstable and showed a small drift during the measurements in the presence of NO_2 at high concentration (540 ppm), demonstrating the

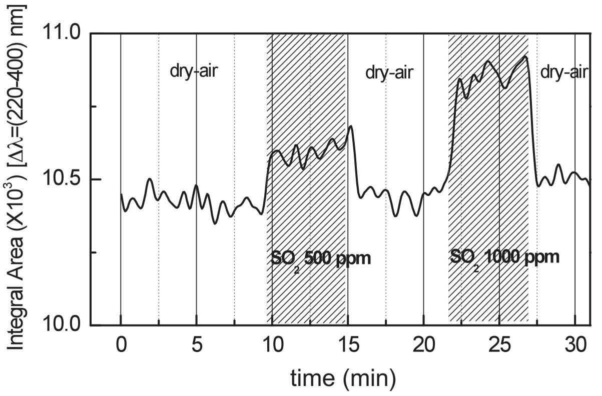

Figure 7 Optical sensing response carried out at a wavelength spectral range $\Delta\lambda$ = (250–400) nm corresponding to the absorption peak of the thin sensing layer versus dry-air, and a mixture containing different SO_2 concentration in dry-air.

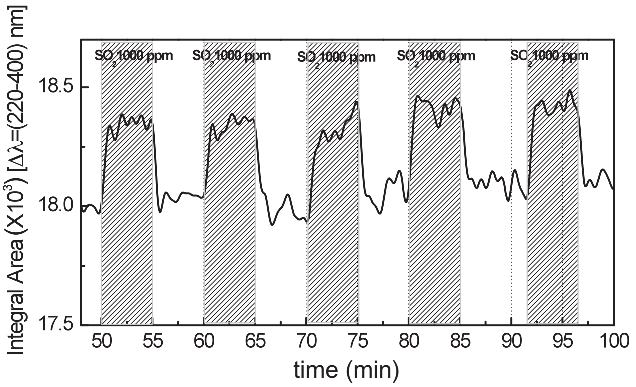

Figure 8 Optical sensing response of thin film versus dry-air and a mixture containing 1000 ppm of SO_2 in dry-air.

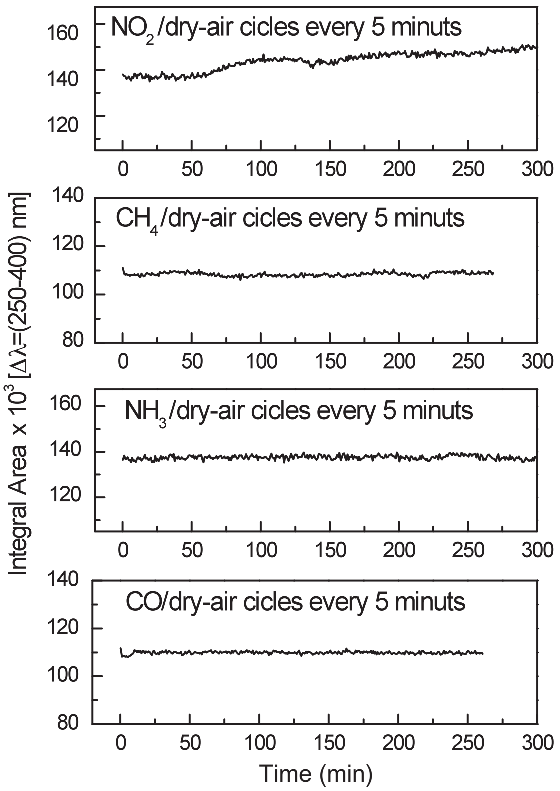

Figure 9 Optical gas sensing responses of the investigated material to NO_2, CH_4, NH_3, CO cycles spaced out by dry air cycles. No optical gas response can be evidenced.

unusability of this material for NO_2 gas sensor application. Moreover, Fig. 9 also reports the response in the presence of NH_3, CO and CH_4 mixture in dry air. As one can see, no variation in the optical response of the investigated sensing material can be evidenced in the investigated spectral range. This indicated a potential selectivity towards SO_2 gas in a mixture with dry-air for this class of materials. Obviously, testing in the presence of mixtures containing interfering gases has to be performed and, in the same time, it is necessary to change the deposition parameters of this thin sensing layer to increase the sensing performance in terms of sensitivity threshold and signal to noise ratio.

4. Conclusion

In this work, we performed a first attempt to use a new organic material in thin film form as active layer in optical gas sensors for various air pollutant gases. The investigated bispyrazole-based thin film shows an interesting sensitivity and selectivity to SO_2 gas with a good reversible response, which opens for us many areas to be investigated. At room temperature, our compound should be potentially suitable as a sensitive material for the development of a simple, low cost and low power consumption optical sensor.

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References

Akila, R., Jacob, K.T., 1989. Sens. Actuators, B 16, 311–323.

Bach, U., Lupo, D., Comte, P., Moser, J.E., Weissörtel, F., Salbeck, J., Spreitzer, H., Grätzel, M., 1998. Nature (London) 395, 583–585.

Banerjee, I., Marek, J., Herchel, R., Ali, M., 2010. Polyhedron 29, 1201–1208.

Beche, B., 2010. Int. J. Phys. Sci. 5, 612–618.

Bouabdallah, I., Touzani, R., Zidane, I., Ramdani, A., 2007. Catal. Commun. 8, 707–712.

Brunet, J., Parra Garcia, V., Pauly, A., Varenne, C., Lauron, B., 2008. Sens. Actuators, B 134, 632–639.

Choi, S.-D., Chung, W.-Y., Lee, D.-D., 1996. Sens. Actuators, B 35–36, 263–266.

Cleary, P.A., Wooldridge, P.J., Cohen, R.C., 2002. Appl. Optics 41, 6950–6956.

De Oliveira, L.L., Campedelli, R.R., Kuhn, M.C.A., Carpentier, J.-F., Casagrande Jr., O.L., 2008. J. Mol. Catal. A: Chem. 288, 58–62.

Gatjens, J., Kampf, J.W., Pecoraro, V.L., 2009a. Inorg. Chim. Acta 362, 878–886.

Gatjens, J., Mullins, C.S., Kampf, J.W., Thuery, P., Pecoraro, V.L., 2009b. Dalton Trans. 8, 51–62.

Guanghua, T., Chuanlong, X., Litang, S., Bin, Z., Daoye, Y., Qi, P., Shimin, W., 2009. Meas. Sci. Technol. 20, 1–8.

Gubillas, A.M., Lazaro, J.M., Conde, O.M., Petrovich, M.N., Lopez-Higuera, J.M., 2009. Sensors 9, 490–502.

Imanaka, N., Yamaguchi, Y., Adachi, G., Shiokawa, J., 1987. J. Electrochem. Soc. 134, 725–728.

Kumar, A., Mehtab, S., Singh, U.P., Aggarwal, V., Singh, J., 2008. Electroanalysis 20, 1186–1193.

Li, H.-F., Han, H.-M., Wu, Y.-G., Xiao, S.-J., 2010. Appl. Surf. Sci. 256, 4048–4051.

Massari, A.M., Gurney, R.W., Wightman, M.D., Huang, C.-H.K., Nguyen, S.T., Hupp, J.T., 2003. Polyhedron 22, 3065–3072.

Mechery, S.J., Singh, J.P., 2006. Anal. Chim. Acta 557, 123–129.

Miller, B., Rosamilia, J.M., Dabbagh, G., Tycko, R., Haddon, R.C., Muller, A.J., Wilson, W., Murphy, D.W., Hebard, A.F., 1991. J. Am. Chem. Soc. 113, 6291–6293.

Scarpellini, M., Wu, A.J., Kampf, J.W., Pecoraro, V.L., 2005. Inorg. Chem. 44, 5001–5010.

Seker, F., Meeker, K., Kuech, T.F., Ellis, A.B., 2000. Chem. Rev. 100, 2505–2536.

Sessler, J.L., Gale, P.A., Cho, W.-S., 2006. Anion Receptor Chemistry. The Royal Society of Chemistry, Cambridge.

Sheu, S.-C., Tien, M.-J., Cheng, M.-C., Ho, T.-I., Peng, S.-M., Lin, Y.-C., 1995. J. Chem. Soc., Dalton Trans.: Inorg. Chem. 21, 3503–3510.

Sigoli, F.A., Messddeq, Y., Ribeiro, S.J.L., 2008. J. Sol–Gel Sci. Technol. 45, 179–185.

Spadavecchia, J., Ciccarella, G., Valli, L., Rella, R., 2006. Sens. Actuators, B 113, 516–525.

Tsiulynu, D., Stratan, I., Tsiulyan, A., Liess, H.-D., Eisele, I., 2007. Sens. Actuators, B 121, 400–413.

Wu, F., Tian, W., Zhang, Z., Ma, Y., Li, G., Shen, J., Zhang, L., Zhang, B., Cao, Y., 2000. Thin Solid Films 263, 214–217.

Xu, Z., Chen, L.-M., Yang, G., Huang, C.-H., Hou, J., Wu, Y., Li, G., Hsu, C.-S., Yang, Y., 2009. Adv. Funct. Mater. 19, 1227–1234.

Yan, Y., Shimizu, Y., Miura, N., Yamazoe, N., 1994. Sens. Actuators, B 20, 81–87.

Yang, P.H., Yang, J.H., Chen, C.S., Peng, D.K., Meng, G.Y., 1996. Solid State Ionics 86–88, 1095–1099.