INTRODUCTION

Increasing pollution due to vehicular traffic and industrial activities is a major problem nowadays, particularly in large urban or industrial areas. Widespread air quality monitoring is mandatory to ensure healthy living conditions. Actually available real-time VOC monitoring systems for in-field environmental monitoring applications are bulky and expensive, being automatic high-end systems derived from laboratory instrumentation. Simple low-cost Thin-film Metal Oxide Semiconductor (MOX) gas sensors characterized by high sensitivity and fast response were recently proposed. Despite their well-established use, some potential applications of MOX are still out of reach due to their low selectivity, low steady state stability, and their temperature dependent behavior. Indeed, the lack of selectivity of MOX gas sensors is one of the major issues in applications where single analytes within complex mixtures must be detected and quantified.

In this work, novel vacuum evaporated thin films based on quinoxaline-bridged cavatand, named QxCav \([C_{11}H_{23}, H]\) (see Figure 1) have been produced. QxCav cavatand has been synthetized at D.C.O.I. of University of Parma purposely for selectively detecting aromatic compounds at very low concentrations (ppb). This is really important taking into account that exposure to aromatic VOCS (benzene in particular) has serious health effects also at low concentrations: in particular breathing high levels of benzene can result in death, while low levels can cause drowsiness, dizziness, rapid heart rate and unconsciousness. The US Department of Health and Human Services (DHHS) classifies benzene as a human carcinogenic. Long-term exposure to high levels of benzene in the air can cause leukemia. In this work thin films of QxCav cavatands have been produced for the first time at Material Laboratories of LNL-INFN via highly vacuum evaporation (VE) technique.

Moreover, insoluble compounds cannot be deposited by such solution techniques: usually, at this purpose, they are decorated with peripheral alkyl chains to improve their solubility. Nevertheless this molecular derivatization introduces dispersion interactions that dilute or even completely obscure the specific analyte response, significantly decreasing sensor selectivity. In particular the use of alkylic chains increases unspecific interactions with all the apolar organic substances.

High-vacuum evaporation (VE) overcomes solubility
problems, allowing for the direct formation of films from solid materials. The lack of residual solvent during the deposition process assures the formation of high purity films: this represents a basic requirement in the gas sensing field, because of the unpredictable effects of the retained solvent on the final response of the sensor, including occupation of adsorption sites and interference in analyte/material interactions. In this regard, recent studies have demonstrated that vacuum-evaporated thin films exhibit higher gas sensing capabilities toward alcohol vapors than chemically deposited films [5,6].

Moreover, VE technique is characterized by good reproducibility, high uniformity, and homogeneity and provides accurate control over both the growth rate and the final thickness of the samples.

**RESULTS AND DISCUSSION**

This paper reports the preliminary results in developing innovative QxCav based VE sensors for selective and sensitive benzene monitoring.

QxCav is a quinoxaline-bridged cavitand featuring a cavity of 8.3 Å deep and 8.0 Å wide, which selectively binds aromatic guests via CH-π interactions with the cavity bottom and walls. In particular the complexation properties of QxCav towards aromatic compounds have been demonstrated both in the gas phase and in the solid state. The nature of bridging groups in this molecule controls the shape and dimension of the cavities, as well as the selectivity in complexation via a combination of shape complementarity and CH-π interactions. QxCav is totally insensitive to aliphatic hydrocarbons, water and to polluting gases present in air like CO, SOx, NOx [7,8,9]. The role of the cavitand’s cavity depth and shape has been studied via theoretical calculation, in particular complexation ability toward small volatile aromatics of the QxCav. The QxCav@benzene complexes are stabilized by weak attractive host-guest interactions involving π electrons of the host, with two C-H guest bonds aligned along the direction of the π orbital of the interacting Chost resorcinarene atoms.

For exploitation as sensing materials, QxCav has been up to now deposited as thin solid film through spin coating technique. Nevertheless this deposition technique is affected by the common drawbacks of standard wet technique previously described (uncontrollable thickness and compact structures or lowering of selectivity due to the presence of molecular derivatizations).

In this work VE technique was used for producing QxCav-sensing coatings. Because this is the first time that QxCav solid films have been deposited by VE, an in-depth characterization of the deposition process and of the properties of the samples is necessary. The deposition rate of the cavitand molecules as a function of crucible temperature by in situ QCM was analyzed in order to individuate the optimal temperature and pressure ranges: the VE films following described were produced at T = 380°C, P = 1.6×10⁻⁴ Pa.

Fourier transform infrared (FT-IR) analyses were moreover performed to investigate the purity of the sublimated films and to exclude the presence of impurities derived from cavitand decomposition (see figure 2).

![FT-IR spectra of vacuum evaporated films (VE) of QxCav. The spectra of the starting powders pressed in KBr pellet (KBr) are also reported as reference.](image)

Vacuum evaporated QxCav thin films show all the characteristic peaks of the starting powders, indicating the absence of damaged molecules in the VE samples, within the detection limits of the techniques employed. Moreover, the lack of any additional peaks in the FT-IR spectra excludes the presence of extraneous compounds, demonstrating the high purity of the samples.

These results are in agreement with previous works [10] and demonstrate the viability of the VE technique for the deposition of thermally stable supramolecular receptors. In the future, the sensing capabilities of the samples towards benzene in low concentrations will be tested and compared to those of standard wet produced samples.