



école doctorale sciences pour l'ingénieur et microtechniques

Development of a silicon micro-device dedicated to the selective detection of VOCs in indoor air: contribution of the "GLAD" technique for the elaboration of nano-structured SnO₂ sensitive layers.

Host institution: Université de Bourgogne Franche-Comté
Laboratory: FEMTO-ST Institute
Domain: Engineering
Discipline: Material chemistry – Applied Physics
Doctoral school: Sciences physiques pour l'ingénieur et microtechniques - SPIM - ED 37

Description of the PhD thesis:

The quality of the indoor air within buildings is a topic of major importance for public health. Among the numerous chemical compounds that can be found in indoor air, formaldehyde and BTEX (benzene, toluene, ethylbenzene and xylene) are considered as one of the most toxic volatile organic compounds (VOCs). In this context, the goal of this study is to develop and deeply characterize an *in-situ* micro-device able to identify and quantify these chemical compounds in indoor air. A silicon micro-preconcentrator, a silicon gas chromatographic micro-column and a semiconductor based chemiresistor gas sensor will compose this analytical micro-system.

The main contributions in this thesis concern on one hand the identification and characterization of suitable porous adsorbents allowing the concentration of indoor air pollutants and, on the other hand the synthesis of nano-structured metal oxides (SnO₂) using an original deposition technique.

For the micro-preconcentrator, several microporous materials with various porosity scales and chemical functions will be considered in order to evidence their adsorption/desorption capacities of various indoor air pollutants.

Concerning the sensing unit of the micro-device, this study will focused on the use of tin oxide-based gas sensor due to their rapid response, stability over the time, easy to use and small size. In particular, the preparation of sensing materials with grain size and porosity in the nanometer range is of technological importance in order to improve the sensing performance. An original approach to obtain well-adjusted metal oxide architecture is to combine two physical vapor deposition techniques based first on a pulsing injection of the reactive gas during the deposition and second focused on the "GLAD" (Glancing Angle Deposition) technique, which enables structuring various architectures. The idea of this study is to develop new nanostructured materials based on tin oxide with unexplored features, especially for gas sensors. These active layers will be deposited on micro-hotplate to produce micro-chemical gas sensors.

The team of supervisors gathers all the know-how to be assembled for this project.







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Work program:

The aim of this PhD is to synthesize and characterize various materials (adsorbents and metal oxide materials) and then to evaluate the detection performances of the micro-device for the identification of indoor air pollutants such as formaldehyde and VOCs.

The work to be done will initially consist in identifying and characterizing well-defined hierarchical materials with controlled porosities, morphologies, surface chemistries in order to evaluate their adsorption/desorption capacities of indoor air pollutants. Zeolites and metal organic frameworks (MOFs) will be considered in this study. Second, the work will deal with the synthesize and characterization of various nanostructured SnO₂ thin films with adjustable compositions using reactive sputtering/GLAD techniques. This should allow us first to evaluate the physical properties (electrical conductivity, thickness ...) of thin films as a function of the deposition parameters and then to select the best parameters for sensing films fabrication. Then, metal oxide materials will be deposited on micro-hotplate devices in order to produce miniaturized chemiresistor gas sensors. Finally, experiments under indoor air pollutants will be carried out in order to evaluate the detection performances of the silicon micro-device in terms of sensitivity, selectivity and stability over the time.

Environment:

The FEMTO-ST Institute have several vacuum deposition machines, which are able to prepare thin films of metal oxide by reactive sputtering. GLAD and RGPP methods will mainly be used in this thesis. They will be widely implemented to create metal/oxide periodic structures and various architectures. Lithography techniques available at FEMTO-ST Institute could also be employed to produce pre-structured surfaces in order to deposit nanostructured and well-organized architectures in 3D. The electronic transport properties will be studied via conductivity measurements, mobility and free carrier concentration as a function of temperature by Hall effect.

Current and future collaborations with other laboratories such as LAAS in Toulouse, ICB in Dijon and the Nanotechnology on Surfaces Research Group (CSIC, Spanish Council of Research) in Sevilla will particularly provide some precious helps to get basic information related to the development of microhotplates and structural characteristics of materials (adsorbents and metal oxide thin films).

<u>Keywords</u>: gas sensors, nanostructured surfaces, GLAD techniques, semi-conductor oxides, porous materials, adsorbents

Profile:

We seek candidates with skills in physical-chemistry, surface science, instrumentation, physical properties of nanostructures, semiconductors and structural characterization techniques.

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To apply, candidates should send the following to *Jean-Baptiste SANCHEZ (jbsanche@univ-fcomte.fr)*:

- A cover letter that describes your relevant experience, research interests.

- CV including the names and contact information of 2-3 references





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Scientific production (2013-2018) :

A. Gaddari, <u>F.Berger</u>, M. Amjoud, <u>J.-B. Sanchez</u>, M. Lahcini, B. Rhouta, D. Mezzane, C. Mavon, E. Beche, V. Flaud, A novel way for the synthesis of tin dioxide sol-gel derived thin films: Application to O_3 detection at ambient temperature, Sensors and Actuators B: Chemical, Vol. 176, 811-817, **2013**.

Y. Mohsen, J.-B. Sanchez, F. Berger, H. Lahlou, I. Bezverkhyy, V. Fierro, G. Weber, A. Celzard, J.-P. Bellat, Selection and characterization of adsorbents for the analysis of an explosive-related molecule traces in the air, <u>Sensors and Actuators B: Chemical</u>, Vol.176, 124-131, **2013**.

M. Arab Pour Yazdi, J.-B. Sanchez, E. Monsifrot, P. Briois, F. Berger, A. Billard, Dodecane sensing with the double substituted LaCoO₃ nanowires deposited by reactive magnetron sputtering, Key Engineering Materials, Vol. 543, 192-195, **2013**.

T. Patois, J.-B. Sanchez, F. Berger, P. Fievet, O. Segut, V. Moutarlier, M. Bouvet, B. Lakard, Elaboration of ammonia gas sensors based on electrodeposited polypyrrole—Cobalt phthalocyanine hybrid films, Talanta, Vol. 117, 45-54, **2013**.

Y. Mohsen, H. Lahlou, J.-B. Sanchez, F. Berger, I. Bezverkhyy, G. Weber, J.-P. Bellat, Development of a micro-analytical prototype for selective trace detection of orthonitrotoluene, Microchemical Journal, Vol. 114, 48-52, **2014**.

A Taguett, M. A. P. Yazdi, J.-B. Sanchez, E. Monsifrot, P. Briois, F. Berger, A. Billard, Synthesis and characterization of Ag doped LaCoO3 nanowire sputter-deposited coatings as heavy hydrocarbon sensors, Key Engineering Materials, Vol. 605, 314-317, 2014.

J. Ollitrault, N. Martin, J.-Y. Rauch, <u>J.-B. Sanchez</u>, <u>F. Berger</u>, Improvement of ozone detection with GLAD WO₃ films, Materials Letters, 155, 1–3, **2015**.

J.-B. Sanchez, H. Lahlou, Y. Mohsen, A. Gaddari, **F. Berger**, Sub-ppm detection of ammonia using a microfabricated gas preconcentrator and a room temperature gas sensor, Sensor Letters, Vol. 13, 1–4, **2015**.

B. Naidji, J. Husson, A. Et Taouil, E. Brunol, <u>J.-B. Sanchez</u>, <u>F. Berger</u>, J.-Y. Rauch, L. Guyard, Terpyridine-based metallopolymer thin films as active layer in ammonia sensor device, Synthetic Metals, 221, 214–219, **2016**.

G. Gregis, S. Schaefer, J.-B. Sanchez, V. Fierro, <u>F. Berger</u>, I. Bezverkhyy, G. Weber, J.-P. Bellat, A. Celzard, Characterization of materials toward toluene traces detection for air quality monitoring and lung cancer diagnosis, Materials Chemistry and Physics, 192, 374-382, **2017**.

G. Gregis, <u>J.-B. Sanchez</u>, I. Bezverkhyy, G. Weber, <u>F. Berger</u>, V. Fierro, J.-P. Bellat, A. Celzard, Detection and quantification of lung cancer biomarkers by a micro-analytical device using a single metal oxide-based gas sensor, Sensors and Actuators B, 255, 391–400, **2018**.

X. Xu, M. Arab Pour Yazdi, <u>J.-B. Sanchez</u>, A. Billard, <u>F. Berger</u>, N. Martin, Exploiting the dodecane and ozone sensing capabilities of nanostructured tungsten oxide films, Sensors and Actuators B, doi 10.1016/j.snb.2018.03.190, to be published, **2018**.