In situ ultrasonic characterization of photocatalytic thin films

Supervisors:

Pr. Guy FEUILLARD (guy.feuillard@insa-cvl.fr)

Dr. Julien BUSTILLO (julien.bustillo@insa-cvl.fr)

Dr. Laurianne BLANC (laurianne.blanc@insa-cvl.fr)

Description of the GREMAN Laboratory:

GREMAN, research group on materials, microelectronics, acoustics & nanotechnology, is a joint research laboratory of Tours University and CNRS and INSA Centre Val de Loire. More than 100 people are working in the laboratory including 45 permanent staff. GREMAN's research topics cover all the process from materials to components and systems.

Research topics are focused on five main themes:

- Functional oxides for energy efficiency: combinatory synthesis and nanostructuration.
- Magnetic & optical properties of ferroïc and electronic correlation materials.
- Innovative materials and components for power and RF microelectronics: wide bandgap & porous SCs and their applications.
- Piezoelectric & capacitive micro- & nano-systems for ultrasound transducers and energy conversion.
- Methods and instrumentation for ultrasonic characterization of complex media.

This PhD Thesis will take place at the INSA site of the laboratory, located in Blois France.

Description of the PhD thesis:

Surface Acoustic Wave (SAW) devices generally consist of interdigital transducers deposited on a piezoelectric substrate for electromechanical conversion (Figure 1). The electrical excitation at the resonance of the transducer makes possible to generate, by inverse piezoelectric effect, a surface acoustic wave propagating at the interface between the substrate and the adjacent medium. By direct piezoelectric effect, it is detected on a receiving transducer. Such devices find many applications in the field of electronics and GSM communications because of the simplicity of implementation and their ability to realize simple and powerful filtering systems.

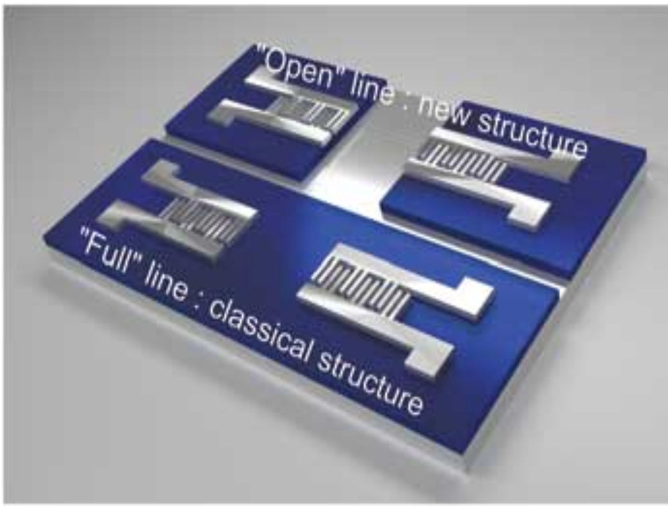

Figure 1: Example of SAW Sensors based on Porous Silicon Layer [3]

Another application of these devices concerns sensors. Indeed the surface wave propagating over a certain distance is able to interact with the external environment. Any modification of this environment will thus modify the characteristics of this wave such as its speed and its attenuation. Measuring the variation of these characteristics therefore provides information on changes in the surrounding environment. With such systems, physical sensors such as humidity, pressure or temperature sensors can be realized.

It is also possible to functionalize the propagation path to make it sensitive to a chemical [1-2] or biological species. This species are adsorbed to the surface and produce a gravimetric effect that will modify the ultrasonic surface wave velocity. The measurement of this speed variation provides information on the amount of chemical or biological species adsorbed.

The sensitivity of such sensors depends in particular on the frequency of the device; generally the operating frequency is in the range 50 MHz 500 MHz. But it also depends on the specific surface of interaction of the surface acoustic wave with the external environment. Larger is the interaction surface higher is the sensitivity. When no treatment is applied the specific surface is equal to the area defined by the transducer width and the distance between the emitter and the receiver. However, if an appropriate treatment is applied, for example by making the surface porous, this surface can be considerably increased. For this reason, the GREMAN laboratory has developed new SAW device using Porous Silicon Layer in order to significantly increase the sensor sensitivity [3].

A previous study conducted by L. Blanc *et al.* have shown that the photocatalytic degradation of pollutants could be monitored during the chemical reaction by measuring the frequency shift of a SAW sensor [4-5] with porous TiO_2 thin films on the propagation path (Fig 2.). Yet, the frequency shift directly depends on the variation of wave celerity and on the pathway length. By assuming that the pathway is invariant, only wave celerity behavior is studied. Its variation depends on two competitive phenomena: a "mass effect" leading to a decrease of the velocity and a "stiffening effect" leading to an increase of the velocity [6]. In addition it has been shown that in case of pollutants adsorption and desorption, both effects occur and cannot be discriminated using frequency shift measurements. Thus only measurement of the film density (ρ) and the Lamé parameters (λ and μ) using an ultrasonic spectroscopy method would allow to more precisely understand the phenomena observed by a SAW sensor during the photocatalytic degradation.

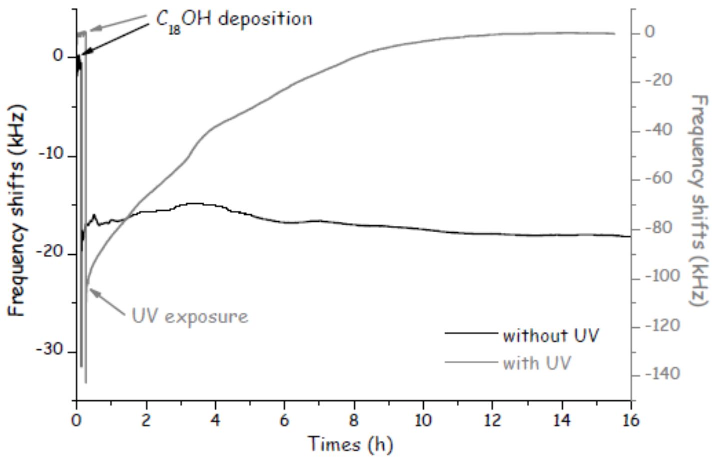

Figure 2: frequency shift observed during the photocatalytic degradation of stearic acid.

The main goal of this thesis is the determination of the film parameters in real time during the SAW measurement to correct the stiffening effect. Doing that, the reaction kinetic could be measured with a higher precision and so be better understood.

In the first step, an analytical model of the SAW sensor has to be developed and implemented to determine the density and the Lamé parameters of the thin film using the ultrasonic spectroscopy. This model has to take account to the porous behavior of the thin film [7], [8]. It will be validated on experiments giving decoupled "mass effect" and "stiffening effect" using SAW sensors manufactured in the GREMAN laboratory.

The second step of this thesis will be the in-situ monitoring of the photocatalytic degradation on a SAW device based on Porous Silicon Layer architecture. The determination of both stiffening and mass effect will be compared to frequency shift measured during the adsorption and desorption in order to obtain corrected reaction kinetics.

Finally these results will be used to optimize the thin film parameters, such as porosity, thickness and formulation, in order to enhance the SAW sensor sensitivity for photocatalysis monitoring.

Candidates should have a Master's degree in Acoustics or Physics. Only candidates with good grades from bachelor and master studies will be considered. Candidates must have good skills in modeling and numerical simulation, as well as a strong taste for experiment.

References :

[1] L. Tessier, F. Patat, N. Schmitt, G. Feuillard, and M. Thompson, "Effect of the Generation of Compressional Waves on the Response of the Thickness-Shear Mode Acoustic Wave Sensor in Liquids," *Anal. Chem.*, vol. 66, no. 21, pp. 3569–3574, Nov.

1994.

[2] G. Feuillard, M. Lethieccl, Y. Janin, L. Tessier, and L. Pourcelot, “Comparative performance of piezoceramic and crystal SAW filters,” *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, vol. 44, no. 1, pp. 194–200, Jan. 1997.

[3] F. Dubosc, L. Blanc, J. Fortineau, and M. Lethiecq, “A Novel Design of Surface Acoustic Wave Device: Towards Sensor Sensitivity Enhancement,” *Sensors Lett.*, 2017.

[4] L. Blanc, “Développement et modélisation de plateformes à ondes acoustiques de surface guidées : caractérisation des propriétés mécaniques de films minces mésoporeux,” 2011.

[5] L. Blanc, A. Tetelin, C. Dejous, D. Rebière, and C. Boissière, “Love Wave Device for Real-Time Monitoring of Pollutant Degradation through Photocatalysis,” in *14th International Meeting on Chemical Sensors - IMCS 2012*, 2012, pp. 927–929.

[6] W. P. Jakubik, “Surface acoustic wave-based gas sensors,” *Thin Solid Films*, vol. 520, no. 3, pp. 986–993, Nov. 2011.

[7] J. Bustillo, J. Fortineau, G. Gautier, and M. Lethiecq, “Ultrasonic characterization of electrochemically etched porous silicon,” *Jpn. J. Appl. Phys.*, vol. 53, no. 6, p. 60308, Jun. 2014.

[8] J. Bustillo, J. Fortineau, G. Gautier, and M. Lethiecq, “Ultrasonic characterization of porous silicon using a genetic algorithm to solve the inverse problem,” *NDT E Int.*, Dec. 2013.