Deliverable 3.6

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Cross-sectorial real-time sensing, advanced control and optimisation of batch processes saving energy and raw materials (RECOBA)

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Report on application of acoustic sensors for real-time properties sensing in batch processes

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Dissimination level

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Content

1 Introduction

The aim of deliverable 3.6 is to provide further information regarding the use of acoustic sensors to identify and monitor the polymer particles during the batch process in light of the work and research done in the last 24 months. The current state, challenges and alternatives for improvement of the three acoustic technologies will be presented in the next sections:

1. Film bulk acoustic wave resonator (FBAR)
2. Surface acoustic wave resonator (SAW)
3. Angular acoustic reflection spectroscopy (AARS)

2 Film bulk acoustic resonator (FBAR)

The use of FBARs as sensors is based on their capacity to vary their resonant frequency when a mass is attached to their surface, also known as gravimetric sensing. One of the key requirements of the resonators fabricated for RECOBA is their capacity to operate in liquid environments. The typical approach to achieve this is to fabricate devices capable of operating in the shear mode (vibration perpendicular to the direction of propagation of the acoustic wave and in the plane of the piezoelectric thin film) because they suffer much lower attenuation in fluids.

Significant advancements in the field of ZnO shear mode resonators have been achieved. Two different methods to deposit ZnO layer with tilted grains (necessary for shear mode operation) have been developed. The first one, using an AlN seed layer of controlled roughness, showed good performance in liquid and was published in M12 [1]. The second method is based on controlling the roughness of the underlying Al bottom electrode and has shown a significant improvement in both performance and reproducibility compared to the first method. The description of this second approach has recently been submitted for publication [2].

With regards to experiments focused on particle monitoring, the detection of polymer particles provided by Polymat using FBARs has been successfully demonstrated, as shown in figure 1.

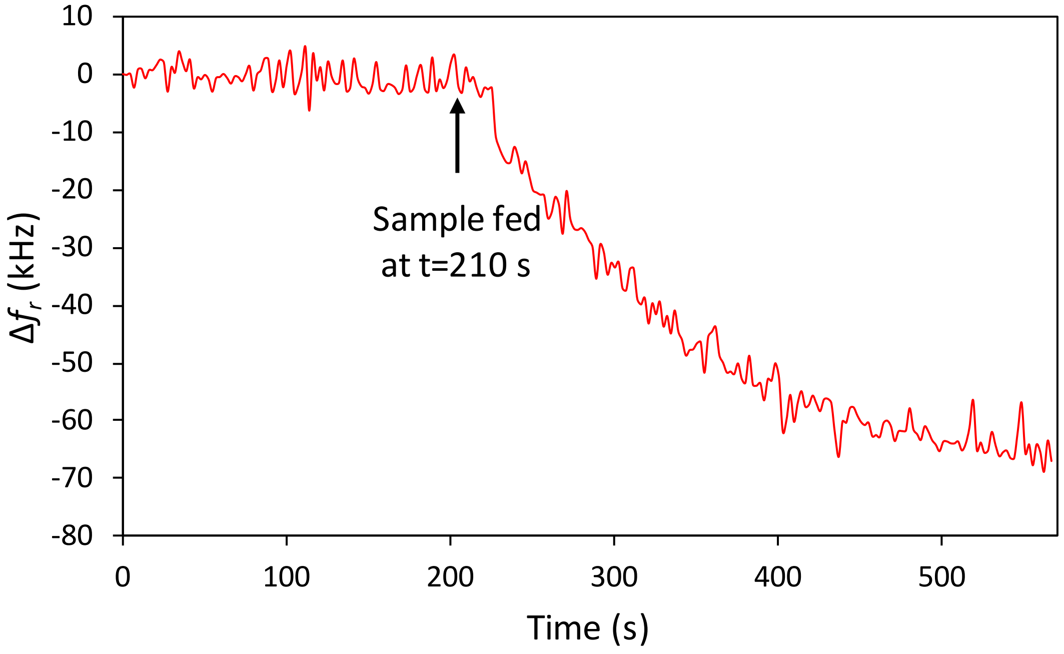

Figure 1 – Evolution of the resonant frequency of the transducer during the polymer particles sensing experiment. When the sample contacts the active area of the device a progressive shift takes place until saturation.

In order to obtain further information about solutions, the sensitivity to viscosity of our devices has been studied. The effect of different water - EtOH mixtures on the resonant frequency of shear mode ZnO resonators is depicted in figure 2.

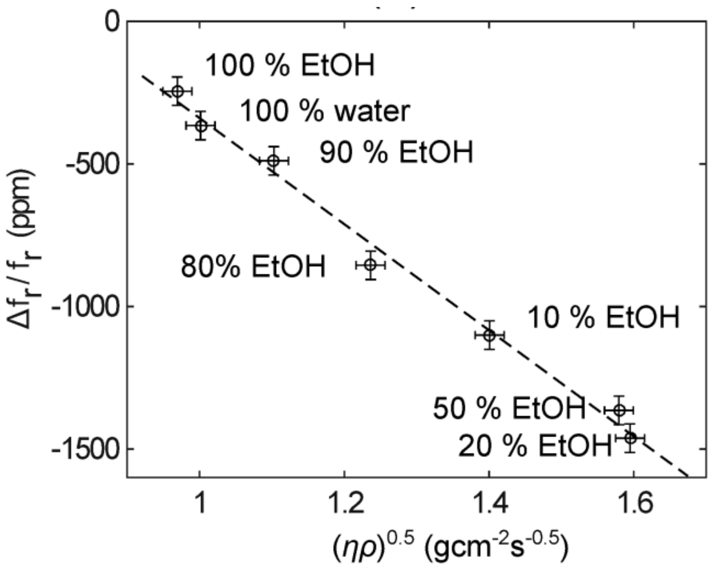

Figure 2 – Evolution of the resonant frequency of the transducer exposed to different water - EtOH mixtures.

In the light of the results, it can be concluded that the information that can be extracted from the solution using the FBARs is the particle presence (and weight of the particles attached to the surface of the resonator) and the viscosity of the liquid. Due to the operating principle of this technology, based on weight variations on the sensing area, the morphological analysis of the particles seems unlikely if no correlation can be found between shape and weight. Taking this into account, two alternatives for improvement can be envisaged:

1. Correlation can be found between weight and shape. In this scenario, an extensive calibration of the devices could permit correlation of the frequency shift with the shape distribution of the particles.
2. The surface of the sensing area and the microfluidic system feeding the solution are engineered to filter the particles arriving at the FBAR sensing surface by their shape.

In any case, both solutions will requiere a major effort and time investment to be explored and there is no guarantee of success. The first option, if feasible, requieres a major calibration of the devices with known solutions containing different particles in different concentrations. The second one is a more interesting and promising approach but involves significant effort and expertise in microfluidics in its development. In addition to this, it could face a potential problem: given the soft character of the particles, the fluidic system or the textured surface could modify their shape, invalidating the method for classification.

3 Surface acoustic wave resonator (SAW)

The second generation of acoustic sensors proposed in RECOBA are SAW sensors. Surface generated wave devices are a much bigger family than FBAR and include many different types of devices. The most important difference between both types of acoustic devices is that the wave generated by the SAW is confined in the surface of the device, instead of in the bulk material as is the case for the FBAR. The generation of the acoustic wave is achieved by the combination of interdigitated transducers (IDTs) and a piezoelectric material. The geometry of the IDTs will determine the electrical response of the SAW device, along with the material properties of the piezoelectric layer and the substrate [3].

The range of choices when using SAW devices is very wide, e.g. geometry of the electrodes, material for the substrate or piezoelectric material. The use of thin film piezoelectric materials such as ZnO or AlN has advantages regarding scalability for commercial purposes (lower price), CMOS compatibility and more flexibility in terms of processing. Therefore, our experiments so far have been focused on SAW sensors with delay line configuration, which consists of two sets of IDTs (input and output) with a space between them (sensing area). We have employed ZnO or AlN as piezoelectric material, silicon as substrate, and fabricated different geometries:

- Pitch: 24 µm, 48 µm.
- Number of finger pairs: 16, 32, 64
- Acoustic aperture: 0.8 mm, 1.2 mm, 1.5 mm
- Wave path: 1.2 mm, 2.4 mm, 4.8 mm, 7.2 mm

Some chips with devices of different geometries used for experiments are shown in figure 3.

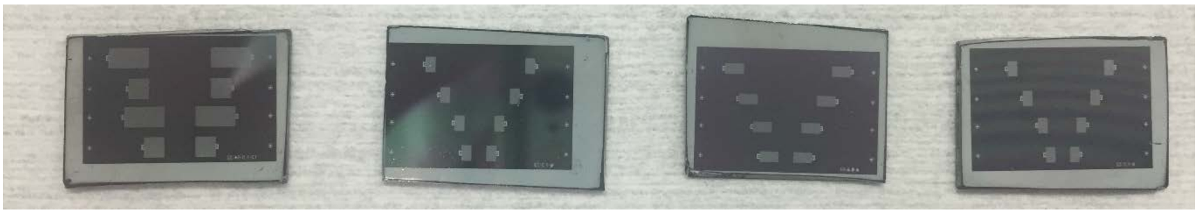

Figure 3 – Chips with SAW delay sensors using different geometries. Each chip contains four different sensors.

The piezoelectric material chosen for the initial test devices was a 4 µm thick ZnO film sputtered on top of a p-type silicon wafer. Further tests were made using AlN as piezoelectric, which has the advantage of withstanding contact with fluids better than

ZnO. In addition to this, the use of high resistivity silicon wafers (ρ > 8000 Ω·cm) enable us to improve the performance and response of the devices by reducing the electrical parasitic elements, as it can be observed in figure 4.

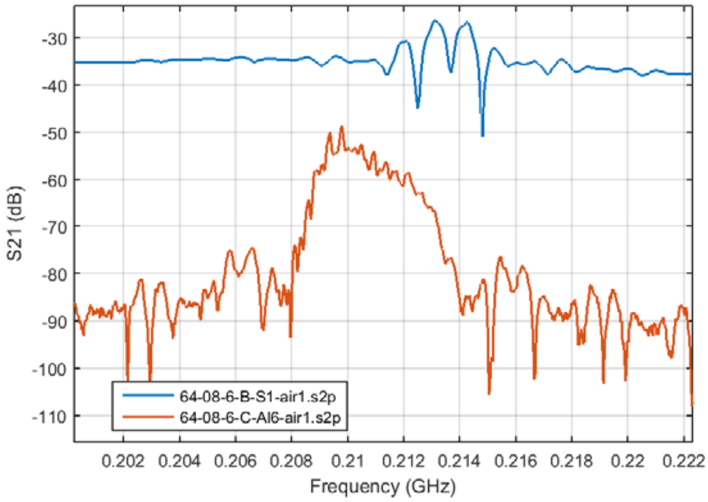

Figure 4 – Response of SAW devices fabricated on p-type/ZnO (S1, solid blue) and high resistivity silicon/AlN (Al6, solid orange). The sinc lobe is much better defined and stronger in the AlN device.

Experiments with solutions containing polymer samples were performed placing 0.5 µl drops on the sensing area of the devices and analysing their response. Different solutions of with 4 different polystyrene beads sizes (100 nm, 200 nm, 300 nm and 460 nm) and 3 different morphologies (spherical, raspberry and multilobe) diluted to 0.5% solids content with DI water were measured in triplicates. Figure 5 displays a sample of measurements using different sizes.

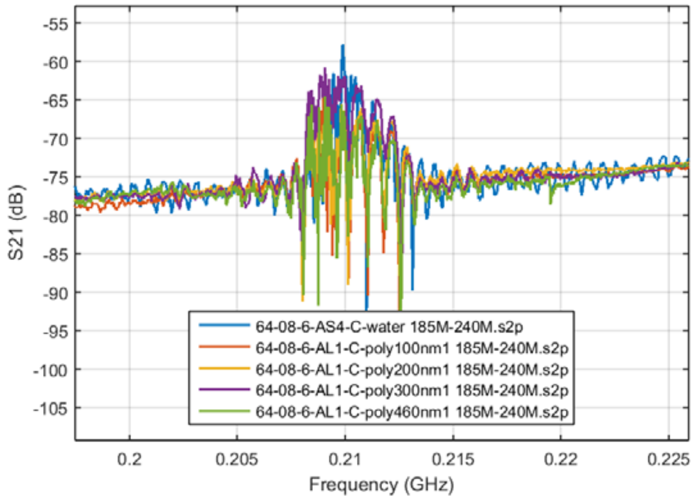

Figure 5 – Response of the SAW devices with drops of water and solutions containing polistyrene beads of 100 nm, 200 nm, 300 nm and 460 nm on the sensing area. No frequency shift can be observed.

The analysis of the measurements reveals that neither the size nor the morphology of the particles cause a resonant frequency shift. Further experiments were performed increasing the sizes of the polystyrene beads up to 10 µm. For the biggest particle, a frequency shift of 100 KHz could be observed, as depicted in figure 6. Solutions with different concentrations of water – EtOH were also measured to analyse the sensitivity to viscosity, but the damping of the signal made it difficult to distinguish any shift in frequency.

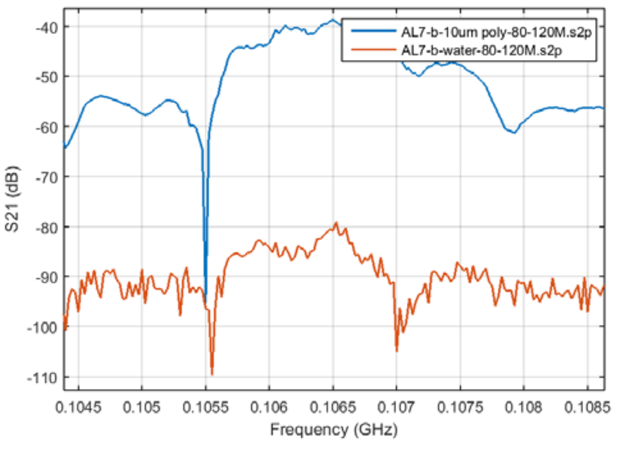

Figure 6 – Response of the SAW sensor exposed to water and to a solution containing 10 µm polystyrene beads. The shift of 100 kHz can be clarly seen in the borders of the principal lobe of the sinc.

In the light of the experiments performed some conclusions can be drawn:

- The damping of the response in liquid makes it very difficult to determine the resonant frequency and to observe any shifts. The structure of the thin films, both AlN and ZnO, only allow the excitation of the Rayleigh mode, which suffers very high degradation in liquids. A novel approach has been tried using layers of AlN with tilted c-axis, but the sensors did not show any mode (e.g. shear) that keeps an acceptable signal when exposed to liquids. To overcome this challenge new materials and different types of devices will be required (e.g. Love Mode Sensors [4]), therefore renouncing to the advantages of using thin films.
- The frequency of the SAWs that are being used is not high enough to detect size variations in the range of nanometres. The current wavelength is in the micrometre range, going down to nanometres will require an increase in frequency (GHz range) which cannot be achieved without a major technological challenge (definition of sub-micron IDTs) and would probably demand outsourcing the fabrication.
- The difficulties to observe viscosity changes in the liquid can be overcome using devices more suitable for in liquid operation (e.g. Love Mode) as it has been demonstrated before [5].

4 Angular acoustic reflection spectroscopy (AARS)

The third technology proposed for the analysis of particles is based on fabricating an array of detectors and an acoustic generator on the same substrate using high resolution patterning and piezoelectric thin films. When the travelling acoustic wave interacts with the target particles, the ultrasonic angular reflection characteristics analysed in the frequency domain will provide information about both the distribution of particle sizes and morphology.

AARS is the most promising technique to successfully fulfil the requirements of RECOBA, but at the same time is the most complex, unexplored and risky approach. The feasibility of this technique has been already tested in finite element analysis simulations using COMSOL Multiphysics ®. These results revealed that AARS is useful to obtain some morphological information from microbubbles in liquid media with a size of 10 µm of diameter.

In the last months additional work has been carried out towards a first version of the AARS sensor. The first approach will use the fluidic chip and holder that is being developed for the in-situ transmission electron microscopy system. The fluidic channels are adequate for this case too, and reusing a similar design with acoustic sensors integrated on them has the additional advantage of sharing the development process and tests. In addition to this, the thickness of the channel (approximately 1 µm) is way below the penetration depth of the longitudinal acoustic wave in the highest frequency that would be necessary for the detection of the smallest particles (4.4 µm at 15 GHz for 100 nm particles).

Despite the advantages of the chosen approach for this first test device, the challenges of its practical implementation that have already been discussed in previous deliverables still remain. The RECOBA projects requires the analysis of particles much smaller than 10 µm, with sizes ranging 100 nm – 400 nm of diameter. This involves higher frequencies of operation, which leads to many complications not only in the fabrication but also in the performance and generation of the acoustic wave. If we consider that the acoustic wave will be generated using an FBAR device, the increase in frequency requires thinner piezoelectric films and therefore implies higher acoustic losses. Simulations of transducer performance using ad-hoc software programmed in Matlab and Comsol indicate that the devices needed for the AARS morphological analysis of particles with a size below 300 nm diameter will not be operational. Above that size, the identification could be feasible, but the difficulties regarding the integration of the system with a very confined microfluidic channel will still be present. A possible alternative that can be explored is the use of different and novel piezoelectric materials with better electromechanical performance, for example AlScN. Despite the inherent difficulties of this technology and the limited chances of complete success regarding its implementation by the end of the project, the AARS technique is still the technology that could respond more comprehensively to the needs of RECOBA and any advance in the area will also represent a very interesting and novel advance in the field of acoustic wave sensors.

5 Conclusions

As a summary of this deliverable 3.6 (M24), we can conclude the following:

- FBAR devices can detect the particles and viscosity changes in the fluid, but are not likely to provide information about their morphology. Different approaches are suggested to obtain more information, but require a major effort and time investment with an uncertain outcome.
- SAW devices, in their current form, are severely attenuated in liquids and cannot detect variations of the particle size and morphology. The challenge of in liquid operation can be overcome renouncing to the advantages of thin films, but the increase of frequency needed to detect size variations in the range of nanometres faces major technological challenges.
- AARS technique could be key to obtain morphological information of particles bigger than 300 nm. The first test devices will be integrated in a system based on the TEM fluidic chip, which has a thickness in the range of the penetration depth of the acoustic waves, necessary to ensure their interaction with the particles. The fabrication still presents many challenges, but the development of both the TEM chip and the AARS sensor and fluidic cell can be developed in parallel.

6 References

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