UNIVERSIDAD POLITÉCNICA DE MADRID

Escuela Técnica Superior de Ingenieros de Telecomunicación

THIN FILM ELECTROACOUSTIC RESONATORS
FOR PHYSICAL AND CHEMICAL SENSING

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Teona Mirea

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Author:

Teona Mirea

Ingeniera de Telecomunicación

Advisors:

Dr. Enrique Iborra Grau

Catedrático del Dpto. de Ingeniería Electrónica

Universidad Politécnica de Madrid

Dra. Jimena Olivares Roza

Profesora Titular del Dpto. de Ingeniería Electrónica

Universidad Politécnica de Madrid

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Contents

Acknowledgements.....	v
Abbreviations.....	vii
Preface.....	ix
Abstract.....	xi
Resumen.....	xiii
Publications.....	xv
1. Introduction.....	1
1.1. Electroacoustic devices	4
1.1.1. Piezoelectricity	4
1.1.2. Acoustic waves in solids	5
1.1.3. Types of electroacoustic devices	6
1.1.4. Thin film electroacoustic devices	10
1.2. Figures of merit of sensors	13
1.3. State of the art in electroacoustic sensors.....	14
1.3.1. Gaseous environments.....	15
1.3.2. Liquid environments.....	17
1.3.3. Harsh environments.....	18
1.4. Objectives and organization of the thesis.....	18
Bibliography.....	20
2. Fundamentals and modelling of electroacoustic resonators.....	29
2.1. Butterworth Van Dyke's model	30
2.1.1. Effective electromechanical coupling coefficient (k_{eff}^2)	33
2.1.2. Quality factor (Q)	33
2.2. Mason's model	34
2.2.1. Electrical impedance derivation	40
2.2.2. Reflector design.....	40

2.3. Finite element analysis	43
Bibliography	46
3. Fabrication and characterization techniques	49
3.1. Fabrication techniques.....	49
3.1.1. Sputtering deposition.....	49
3.1.1.1. High vacuum systems.....	50
3.1.1.2. Ultra-high vacuum system: AlN growth	51
3.1.2. Chemical vapor deposition for CNT growth	52
3.1.3. Device fabrication routes.....	54
3.1.3.1. Lamb wave resonators.....	54
3.1.3.2. Solidly mounted resonators	56
3.2. Characterization techniques	57
3.2.1. AlN characterization.....	57
3.2.1.1. X-Ray diffraction	58
3.2.1.2. Fourier transform infrared spectroscopy	60
3.2.1.3. Assessment of the film stress	61
3.2.2. Electrical characterization of resonators.....	62
3.2.3. CNT characterization	64
3.2.3.1. Atomic force microscopy	64
3.2.3.2. Scanning electron microscopy	65
3.2.3.3. Raman spectroscopy	65
3.3. Device applications: measurements set-up.....	67
3.3.1. In-liquid testing of S_0 -LWRs (comparison with shear-SMRs).....	67
3.3.2. SMRs characterization at high temperatures	69
3.3.3. SMRs with integrated CNT forests: gas sensing applications.....	71
Bibliography.....	73
4. S_0 mode Lamb wave resonators for in-liquid applications.....	77
4.1. In-liquid behavior predicted by FEM modelling.....	78
4.1.1. Liquid model	80
4.1.2. FEM analysis results	82
4.1.2.1. Mechanical sensing (density and viscosity)	82
4.1.2.2. Electrical sensing (dielectric permittivity)	87
4.1.2.3. Influence of the membrane thickness on the sensing performance	89

4.2. Theory vs. experiments: FEM model validation	93
4.2.1. Mechanical sensing (density and viscosity)	95
4.2.2. Electrical sensing (dielectric permittivity)	98
4.3. S_0 -LWRs vs. shear FBARs for in-liquid applications	99
4.3.1. Comparison considerations: FBARs, SMRs, and S_0 -LWRs	103
4.4. Summary	107
Bibliography.....	108
5. CNT-based solidly mounted resonators: high temperature applications	
and gas sensing	111
5.1. SMRs for high temperature processing	112
5.1.1. Device design	112
5.1.1.1. Acoustic reflector	113
5.1.1.2. AlN film	116
5.1.2. SMR performance after high temperature annealing	116
5.1.3. SMR in-situ performance at high temperatures.....	120
5.2. Growth of carbon nanotube forests	123
5.2.1. CNT growth on piezoelectric AlN	125
5.2.2. CNT growth on metallic films.....	132
5.3. Integration of CNT forests on SMRs	137
5.3.1. Fabrication route.....	137
5.3.2. Influence of CNT forests on the device performance.....	138
5.4. Gravimetric detection using CNT-based SMRs	142
5.5. Summary	144
Bibliography.....	146
6. Conclusions and future work	151
6.1. Conclusions	151
6.2. Future work	153
Bibliography.....	155

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Abbreviations

EA	Electroacoustic
TEA	Thin Film Electroacoustic
QCR	Quartz Crystal Resonator
QCM	Quartz Crystal Microbalance
BAW	Bulk Acoustic Wave
SAW	Surface Acoustic Wave
FBAR	Film Bulk Acoustic Resonator
SMR	Solidly Mounted Resonator
LWR	Lamb Wave Resonator
S ₀ -LWR	S ₀ mode Lamb Wave Resonator
IDT	Interdigital Transducer
CNT	Carbon Nanotube
SWCNT	Single Wall Carbon Nanotube
MWCNT	Multi Wall Carbon Nanotube
CVD	Chemical Vapor Deposition
NP	Nanoparticle
AFM	Atomic Force Microscopy
SEM	Scanning Electron Microscopy

Preface

This thesis is the result of my four research years within the Microsystems and Electronics Materials Group (GMME, from its Spanish version *Grupo de Microsistemas y Materiales Electrónicos*) at the Telecommunications Engineering Faculty from the Technical University of Madrid. As the thesis title suggests, all efforts were focused on the final development of thin film electroacoustic sensors. I would like to emphasize, with these first words, that the journey to reach something close to an operative sensor was not short, neither easy. Exhaustive research had to be done first on the materials and their proper integration in the devices. With the support of the extensive knowledge of the group on materials development and applications, I have tried to give actual sensing applications to AlN-based resonators. This includes studying their behavior in new or non-standard environments and integrating new materials, always having in mind the feasibility of industrialization. Although brought together under the same theme – “Thin film electroacoustic sensors” – the work I have carried out these years has rewarded me with knowledge in three different fields: the sensing mechanisms of S_0 mode Lamb wave resonators (S_0 -LWRs), particularly in liquid environments, the adaptation of solidly mounted resonators (SMR) for very high temperature applications, and the growth of carbon nanotube (CNT) forests on different substrates for their integration on the resonators.

In the first case, the aim was to study the performance of the relatively new LWRs in liquid environments, especially working on their less exploited S_0 mode. This was considered having in mind their potential for industrialization owing to their inherent AlN *c*-oriented nature, compared to their more mature shear mode film bulk resonators counterparts. In this case the finite element simulation and the subsequent experimental validation provided me with a deep insight into the acoustic wave interaction with adjacent media.

In the second case, the need for SMRs sustaining high temperatures first appeared due to their delamination problems when integrating CNT forests on their top active area with the scope of improving their gas sensing performance. The growth of CNTs requires more than 600°C. To adapt the SMR structure, mainly the acoustic reflector, the mechanical stress and the adhesion of the materials were tuned to the optimal conditions. The designed structure proved 100% success for all annealing tests sustaining temperatures up to 700°C. The success of these results also suggests them as an alternative to the widely used LGS-based surface acoustic wave devices for harsh environments applications.

In the last case, the integration of CNT forest as active sensing layers in SMRs required extensive studies on their growth, initially on AlN, but more importantly on the metallic top electrodes of the devices. The direct integration of CNT forest instead of their typically used dispersed or in composite forms was proposed for improving the surface area for functionalization. Initially their growth was studied on AlN substrates because CNTs, owing to their unique electronic and chemical properties, were proposed to act simultaneously as top electrodes and sensing layers. However, this idea did not result practical from the device performance point of view, hence was solved by integrating the CNTs on the metallic top electrodes. The growth of CNTs on metallic substrates is not straightforward owing to the diffusion of the catalytic metals, which form nanoparticles to promote CNT growth, into the bulk of the metallic substrate. High quality single-walled CNTs were grown on different metallic films by using a metallic barrier layer between catalyst and substrate and by tuning the nanoparticle formation temperature.

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The last one (IC1208 COST Action) funded the two short term scientific mission (two-months each) I performed at Uppsala University and Cambridge University. At Uppsala University, where the fabrication of the LWR devices was finished, I gained knowledge on S_0 -LWRs and finite element simulations; and at Cambridge University I expanded my know-how on the growth mechanisms of CNTs.

Abstract

The fields of application of sensing devices are constantly expanding. From industrial processes monitoring to food quality control, sensors play a key role as information collectors, essential for human safeness, costs reduction and efficiency improvement. Their impact is even more pronounced in fields like the healthcare one, where biosensors have become crucial for prognosis and early diagnosis. As a result, high performance, low cost and reliable sensors are more and more demanded. In this context thin film electroacoustic sensors offer high resolution, high sensitivity, simplicity, low size, low manufacturing costs and possibility for array integration. Among this class of devices, thin film bulk acoustic wave resonators (FBARs), and more recently, Lamb wave resonators (LWRs) have attracted considerable attention. In both cases, although their sensing performance in different environments, namely gaseous and liquid, have been already studied, they have still unexplored features or improvement possibilities. This thesis aims at contributing to the field of thin film electroacoustic sensors by expanding the physical and chemical sensing features of AlN-based FBARs, particularly solidly mounted resonators (SMRs), and S_0 mode LWR (S_0 -LWRs).

On one hand, Lamb wave devices exploiting the A_0 mode, generally in delay line structures, have been widely studied in terms of their mass (gravimetric), but more deeply, of their in-liquid sensing mechanisms. However, the S_0 mode is a potential candidate for in-liquid operation owing to its strong extensional component, which prevents radiation to the liquid. AlN-based S_0 -LWRs are relatively new devices and, although their gravimetric performance has been already studied, their sensing mechanisms in liquid environments have not been fully explored yet. Compared to FBARs that require tilted grains for their operation in liquids, S_0 -LWRs use c -oriented AlN, a deposition process already industrialized. This place them as the most promising candidates for commercialization. In this thesis the in-liquid sensing mechanisms of S_0 -LWRs are simulated through finite element analysis, and experimentally verified. Results show that S_0 -LWRs, in contrast to pure shear mode devices, are slightly more sensitive to the liquid density than to its viscosity. This arises from their different coupling mechanism to the liquid owing to the elliptical polarization, which, besides a strong extensional component, has a small vertical component. Moreover, if their membrane thickness is reduced their sensitivity is improved. Additionally, they are also sensitive to the dielectric permittivity of the liquid. However, a trade-off between technological feasibility and device performance should be always considered. A comparison between S_0 -LWRs and shear mode FBARs shows that S_0 -LWRs are more sensitive to the liquid

mechanical properties when both devices work at the same resonant frequency (900 MHz), but also when FBARs work at higher frequencies (2 GHz).

On the other hand, FBARs, owing to their maturity, have been thoroughly investigated in both gaseous and liquid environments. However, much efforts have been put on the latter leaving their gas sensing potential with unexplored possibilities. In this thesis the integration of carbon nanotube (CNT) forest as sensing layers on AlN-based SMRs is proposed for boosting their gravimetric sensing performance. Vertically-aligned CNTs offer high surface area and a wide chemical affinity, suitable for sensor selectivity improvement. For the integration of CNT forests, two problems are solved in the thesis: SMRs holding high temperatures (CNT growth requires temperatures higher than 600°C), and growth of CNTs on the metallic top electrodes of SMRs. The integrity of SMRs at high temperatures is guaranteed by a design including low stressed materials with high interlayer adherence. The successful growth of high quality CNT forests on metals like Mo or Ir is achieved by combining an Al under-layer with Fe catalyst, and using a temperature for nanoparticles formation lower than the one used for CNT growth. A proof of concept on the gravimetric sensing viability of CNT-based SMRs is demonstrated by detecting ethanol vapors.

Resumen

Hoy en día, los campos de aplicación de los sensores están en continua expansión. Desde la monitorización de procesos industriales, cada vez más automatizados, hasta el control de la calidad alimentaria, los sensores juegan un papel clave como recolectores de información. Su impacto es incluso más pronunciado en campos como el de la sanidad, donde los biosensores se han convertido en dispositivos esenciales para el pronóstico y la detección precoz de enfermedades. Como consecuencia, la sociedad demanda sensores fiables, de alto rendimiento y de bajo coste de forma acuciante. En este contexto los sensores electroacústicos de película delgada ofrecen prestaciones muy adecuadas entre las que destacan una alta resolución, alta sensibilidad, simplicidad de manejo, tamaño reducido, bajos costes de fabricación y la posibilidad de integrarlos en arrays. Entre esta clase de dispositivos, los resonadores de ondas acústicas de volumen de película delgada (FBARs, del inglés *thin film bulk acoustic wave resonators*), y más recientemente, los resonadores de ondas Lamb (LWRs, del inglés *Lamb wave resonators*) han atraído la atención considerablemente en los últimos años. En ambos casos, aunque su rendimiento como sensores en diferentes entornos, como el gaseoso o el líquido, ya ha sido estudiado, aún necesitan ser optimizados en algunos aspectos importantes. El objetivo de esta tesis es contribuir al campo de los sensores electroacústicos de película delgada, expandiendo las características sensoriales físicas y químicas de resonadores basados en películas delgadas de AlN. En particular, se estudian dos tipos de dispositivos, los FBARs basados en espejos acústicos (SMRs del inglés *solidly mounted resonators*), y los LWRs usando el modo S_0 (S_0 -LWRs).

Por un lado, los dispositivos Lamb usando el modo de propagación antisimétrico A_0 han sido extensamente estudiados como sensores de masa (gravimétricos) y como sensores trabajando en medio líquido. Sin embargo, el modo de propagación simétrico S_0 es un candidato con gran potencial para operar en medios líquidos dada su gran componente extensional, la cual impide la radiación acústica al líquido. Los S_0 -LWRs basados en AlN son dispositivos relativamente recientes y, a pesar de que su rendimiento gravimétrico ya ha sido estudiado, su operación en medios líquidos aún no ha sido completamente explorada. En comparación a los FBARs, que necesitan trabajar en modos de cizalladura usando películas con granos inclinados para operar en líquido, los S_0 -LWRs usan AlN con orientación vertical del eje c , cuyo proceso de depósito ya está industrializado. Esto les sitúa como los candidatos más prometedores para ser comercializados en un futuro muy próximo. En esta tesis se presentan los resultados de la simulación por elementos finitos de estos dispositivos (S_0 -LWRs) como sensores de las propiedades de medios líquidos como la densidad, viscosidad o constante dieléctrica. Estas simulaciones se confrontan con medidas experimentales obteniendo muy buena concordancia.

Los resultados demuestran que, al contrario que los dispositivos de modo de cizalladura, los S_0 -LWRs son ligeramente más sensibles a la densidad del líquido que a su viscosidad. Esto es debido al mecanismo de acoplo al líquido del modo S_0 , cuya polarización elíptica, aparte de tener una fuerte componente extensional, también posee una pequeña componente transversal acoplada a ella. Además, si el espesor de la membrana del dispositivo se reduce, su sensibilidad mejora. Adicionalmente, estos dispositivos también son sensibles a la permitividad dieléctrica del líquido. Una comparación entre los S_0 -LWRs y los FBARs en modo de cizalladura demuestra que los S_0 -LWRs son más sensibles a las propiedades mecánicas de los líquidos cuando ambos dispositivos funcionan a la misma frecuencia de resonancia (900 MHz), e incluso cuando los FBARs trabajan a frecuencias mayores (2 GHz).

Por otra parte, los FBARs, debido a su madurez han sido exhaustivamente investigados en medios gaseosos y líquidos. Sin embargo, la mayoría de los esfuerzos se han centrado en su operatividad en líquidos, dejando su potencial como sensores de gas con posibilidades inexploradas. En esta tesis se propone la integración de bosques de nanotubos de carbono alineados verticalmente (CNTs, del inglés *carbon nanotubes*) como capas sensibles sobre SMRs basados en AlN para mejorar su rendimiento gravimétrico. Los CNTs alineados verticalmente ofrecen una gran área y una alta afinidad química después de ser funcionalizados, lo que les hace ideales para mejorar la sensibilidad y selectividad del sensor. Para la integración de los bosques de CNTs se han resuelto dos problemas: la conservación de la integridad mecánica de los SMRs a altas temperaturas (el crecimiento de CNTs requiere temperaturas mayores que 600°C) y el crecimiento de CNTs en los electrodos superiores de los SMRs. La integridad de los SMRs a altas temperaturas se ha garantizado mediante el diseño de una estructura con materiales de bajo estrés y una alta adherencia entre capas. El crecimiento de bosques de CNTs de alta calidad en metales como el Mo o el Ir se ha conseguido mediante la combinación de una capa estabilizadora de Al bajo el catalizador de Fe, y el uso de temperaturas para la formación de nanopartículas menores que las usadas para el crecimiento de los CNTs. Como prueba de concepto, la viabilidad y mejora en prestaciones de sensores de gases basados en SMRs con CNT integrados ha sido demostrada mediante la detección de etanol.

Publications

Articles in peer-reviewed journals

- i. **T. Mirea**, V. Yantchev; *Influence of liquid properties on the performance of S0-mode Lamb wave sensors: A theoretical analysis*, Sens. Actuators, B (208), pp. 212-19, 2015. (IF = 4.101)
- ii. **T. Mirea**, J. Olivares, M. Clement, M. DeMiguel-Ramos, J. de Frutos, J. Sangrador, E. Iborra; *Carbon nanotube growth on piezoelectric AlN films: influence of catalyst underlayers*; RSC Adv. (5), pp. 80682-87, 2015. (IF = 3.84)
- iii. **T. Mirea**, V. Yantchev, J. Olivares, E. Iborra; *Influence of liquid properties on the performance of S0-mode Lamb wave sensors II: Experimental Validation*; Sens. Actuators, B (229), pp. 331-37, 2016. (IF = 4.101)
- iv. J. Olivares, **T. Mirea**, B. Díaz-Durán, M. Clement, M. DeMiguel-Ramos, J. Sangrador, J. de Frutos, E. Iborra; *Growth of Carbon Nanotube Forests on Metallic Thin Films*; Carbon (90), pp. 9-15, 2015. (IF = 6.638)
- v. S. Esconjauregui, T. Makaryan, **T. Mirea**, M. DeMiguel-Ramos, J. Olivares, Y. Guo, H. Sugime, L. D'Arsié, J. Yang, S. Bhardwaj, C. Cepek, J. Robertson, E. Iborra; *Carbon nanotube forests as top electrode in electroacoustic resonators*; Appl. Phys. Lett. (107), pp. 133106-5, 2015. (IF = 3.302)
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- viii. M. DeMiguel-Ramos, **T. Mirea**, J. Olivares, M. Clement, J. Sangrador, E. Iborra; *Assessment of the shear acoustic velocities in the different materials composing a high frequency solidly mounted resonator*; Ultrasonics (62), pp. 195-99, 2015. (IF = 1.94)
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- i. E. Iborra, J. Sangrador, M. Clement, **T. Mirea**, M. DeMiguel-Ramos, J. Olivares, J. Capilla, L. García-Gancedo, S. Esconjauregui, A. J. Flewitt, W. I. Milne; *Acoustic Properties of Carbon Nanotube Electrodes in BAW Resonators*; Proceedings in 2013 Joint European Frequency and Time Forum & International Frequency Control Symposium, pp. 984-87, 2013. **(oral)**
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Conference contributions

- i. **T. Mirea**, J. Olivares, M. Clement, B. Díaz-Durán, J. Sangrador, E. Iborra; *Solidly mounted resonators with integrated carbon nanotube forests for chemical sensing*; Eurosensors XXX Conference, 2016. **(poster)**
- ii. **T. Mirea**, J. Olivares, M. Clement, B. Díaz-Durán, J. Sangrador, E. Iborra; *AlN based-Solidly mounted resonators at high temperatures: In-situ characterization*; 2016 IEEE International Ultrasonics Symposium. **(poster)**
- iii. **T. Mirea**, J. Olivares, M. Clement, M. DeMiguel-Ramos, J. de Frutos, J. Sangrador, E. Iborra; *Carbon Nanotubes Growth on Piezoelectric Thin Films*; 2014 Diamond and Carbon Materials Conference. **(poster)**
- iv. J. Olivares, **T. Mirea**, B. Díaz-Durán, M. DeMiguel-Ramos, J. Sangrador, M. Clement, E. Iborra; *Sheet Resistance Measurements of Carbon Nanotube Forests for Electrodes*; 2014 Diamond and Carbon Materials Conference. **(poster)**
- v. J. Olivares, **T. Mirea**, B. Díaz-Durán, M. Clement, M. DeMiguel-Ramos, J. de Frutos, E. Iborra; *Carbon Nanotubes Growth on Metallic Thin Films*; 2014 Diamond and Carbon Materials Conference. **(poster)**

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for the poster

"S0 Lamb Wave Resonators for in-Liquid Sensing: Promising Alternative to Shear Bulk Acoustic Wave Devices"

Eckehard Peik

Chairman of the EFTF Executive Committee
Eckehard Peik

Patrick Gill

Senior NPL Fellow, Time and Frequency
Patrick Gill

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Chapter 1

Introduction

This chapter describes the operating principles of electroacoustic devices and their application as sensors. It includes a classification of the different types of electroacoustic devices and their state of the art in gas, liquid and harsh environments sensing applications. Finally, the objectives and the organization of the thesis are explained.

Control and continuous monitoring have become crucial strategies for success in many traditional and modern sectors. In this context, sensors have become leading players as information collectors. Many are the applications where such examples can be found. In the industrial sector the control of hazardous agents through chemical sensors [1]–[3], or of lubricants quality through liquid physical sensors [4]–[7], has become essential. Chemical and biochemical sensors have also found extensive applications in food contamination control [8]–[11] or environmental hazardous agents detection [8], [12]–[14]. Another prominent sector is the healthcare one, where prevention and control of diseases are vital for future costs reduction; this can be achieved by monitoring a patient at the nearest point of care or even at home, by simple, fast, and cost effective tests for analysis of proteins, pathogens, or other biochemical species [8], [15]–[17].

These tendencies are promoting a technological innovation and an increasing demand for different types of sensors. An electronic sensor is a device that, in response to an exterior stimulus, provides an electrical output signal, which allows quantifying the stimulus. Such stimulus may be a property, quantity or condition and can be referred to as measurand. Basically, sensors are energy converters specifically classified by the transduction methods they employ. There exists a

1. Introduction

vast variety of such transduction methods, from electrical (resistive, capacitive, inductive, conductive, etc), thermal, optical to acoustical [18], [19]. Depending on the kind of application, a transduction method might be more suitable than another. The emerging applications are continuously demanding more strict requirements to be fulfilled by the sensing devices. These include, higher sensitivity and specificity, lower power consumption, quicker response, miniaturization and, of course, lower cost. One of the most promising transduction methods, able to fulfil the mentioned requirements, is the acoustical one. Acoustic sensors offer high resolution, real time response, simplicity, small size and low production costs. This transduction type is based on the transformation of an input stimulus into an electrical output signal by means of a mechanical (acoustic) wave. This type of waves can be converted to electrical signals through piezoresistive, capacitive or piezoelectric techniques, being the latter the most extensively studied [20], [21]. The core of an electroacoustic (EA) sensor is a piezoelectric transducer, which can be either a delay line or a resonant structure [22], [23]. While the first one is based on the emission and subsequent detection of a travelling acoustic wave, an EA resonator can be thought as a confinement structure for standing acoustic waves at a resonant frequency. The most basic example of an EA resonator is the quartz crystal resonator (QCR) [24] (Fig. 1.1).

Fig. 1.1. Representation of a quartz crystal resonator composed of a piezoelectric (quartz) plate sandwiched between two metallic electrodes.

The QCR is composed of a piezoelectric plate, in this case quartz, sandwiched between two electrodes on which we apply an electric potential difference, inducing thus an electric field inside the piezoelectric material. Thereby, acoustic waves are generated inside. These waves are reflected at the lower and upper quartz-electrode interfaces. In this situation a resonance condition is achieved when the excited and reflected waves interfere in a constructive manner, forming a standing wave. If the constructive interference condition is applied ($d = N \frac{\lambda}{2}$, $N \in$

$\{1, 3, 5, 7 \dots\}$), where λ is the acoustic wavelength, and d the thickness of the quartz plate, then the value of the resonant frequency is defined by:

$$f = \frac{v_{wave}}{\lambda} = N \frac{v_{wave}}{2d} \quad (1.1)$$

where v_{wave} is the velocity of the acoustic wave in the piezoelectric material. When $N = 1$ the resonant frequency is called fundamental frequency (f_0) of the resonant mode, and for $N \neq 1$ we have equally spaced odd harmonics $(2n+1) \cdot f_0$ with $n=1,2,3\dots$

As observed, the resonant frequency is set by the material properties and the geometry of the device structure. Changes in the surrounding medium can perturb the response of EA devices either by affecting the propagation characteristics of the wave or by virtually varying the geometry. For the particular case of EA resonators, this is basically translated to variations in the resonant frequency, which can be monitored by the electrical output signal.

The acoustic wave technology is not new; it has been exploited by the telecom industry over the last 70 years. Its unique features have made EA devices key factors in the fabrication of small, cheap and high-performance band-pass filters [25]–[28]. Billions of EA filters are consumed annually in mobile telecommunication systems (e.g. GSM, UMTS), data transfer technologies (Wi-Fi technologies), consumer electronics (tablets, music players, remote controllers, toys, etc.), or base stations. The maturity gained by the acoustic wave technology in the telecom industry is a great advantage for its application in the sensors field. EA devices are typically based on the surface acoustic wave (SAW) and the bulk acoustic wave (BAW) technologies. Both have been traditionally based on single crystalline piezoelectric materials (e.g. LiNbO_3 , quartz). However, new standards of the telecom industry in terms of monolithic integration, higher frequency of operation, fabrication cost reduction or miniaturization, have dictated new trends in the EA technology. This tendency is certainly a shared scope with the sensors sector. One of the mentioned standards, higher frequency of operation, has been proved to increase the sensor mass sensitivity [29]. Not only have single crystalline piezoelectric materials reached physical limits to attain higher frequencies, but they are also incompatible with monolithic integrated circuits and have high fabrication costs. Their use is restricted if higher miniaturization, higher frequencies, chip integration and batch-processing technologies are pursued. The solution has been the use of thin film piezoelectric materials (e.g. AlN , ZnO), which has been possible due to the strong development of the fabrication and deposition techniques within the microtechnology sector. EA sensors based on thin films have already proved their superior potential compared to their single crystalline counterparts [30]–[32].

1.1. Electroacoustic devices

1.1.1. Piezoelectricity

As introduced, one of the most exploited techniques for the generation of acoustic waves is the piezoelectric effect [21]. Piezoelectricity can be defined as the ability of some materials to generate an electric charge (hence an electric field) when an external stress is applied on them – direct piezoelectric effect – or vice versa, an applied electric field causes a mechanical deformation or strain on them – reverse piezoelectric effect [33], [34]. For that to occur, dipole moments in the material must displace under deformation and create a net polarization variation. This means that, for the existence of piezoelectricity, the structure of the material must possess a crystallographic asymmetry, which generates a non-zero dipolar moment [35]. In other words, piezoelectric materials are electrically anisotropic in their crystal structure. Essentially, what we have is a transducer for turning electrical energy into mechanical energy and vice versa, which can be defined as a linear interaction between an electrical and a mechanical system. Such interaction is described by the piezoelectric constitutive relations, which can be considered a combination of Hooke's fundamental law ($T = cS$) and Maxwell's constitutive equation ($D = \varepsilon E$) [36], [37]:

$$T = c^E S - eE \quad (1.2)$$

$$D = \varepsilon^S E + eS \quad (1.3)$$

Here T is the stress, S the strain describing the deformation of the crystal, E the applied electric field, and D the electric displacement. The material parameters are represented by the stiffness constant (c^E), the piezoelectric stress constant (e) and the permittivity of the material (ε^S). Superscripts E and S denote that c and ε constants must be measured under constant electric field and strain conditions, respectively. The second terms in both equations are the ones related to the piezoelectric effect. The efficiency of a piezoelectric material to convert electrical energy to mechanical, and vice versa, is represented by its intrinsic electromechanical coupling coefficient, which can be expressed in a generic form as [36]:

$$k^2 = \frac{e^2}{c \cdot \varepsilon} \quad (1.4)$$

where e , c and ε are elements of tensors and the value of k^2 depends on the directions considered for the particular system.

Typical piezoelectric materials are quartz, LiTaO_3 , LiNbO_3 or Langasite (LGS), which are bulk single crystalline materials, and $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), ZnO or AlN , which are used in their thin film form [38]. Their specific use is discussed in more detail in the subsequent sections.

1.1.2. Acoustic waves in solids

Once the acoustic wave is generated, we should deal with its propagation characteristics, in this case through a solid. Combining basic relations like Newton's second law ($F = ma$), the definition of particle velocity ($v = \partial u / \partial t$, where u is the particle displacement), the definition of strain ($S = \partial u / \partial z$), and Hooke's law ($T = cS$) leads to the basic one-dimensional equation of a propagating wave in a solid:

$$\frac{1}{\rho} \frac{\partial^2 T}{\partial z^2} = \frac{1}{c} \frac{\partial^2 v}{\partial t^2} \quad (1.5)$$

where ρ is the mass density of the material and z the propagating direction. The solution of this equation is a plane wave with acoustic polarization in the direction of the wave propagation, i.e. a longitudinal or pressure wave with phase velocity $V_{wave} = \sqrt{c/\rho}$ [36].

However, in a more realistic case, this equation should be treated in a three-dimensional system. Then Eqs. 1.2 and 1.3 will adopt the following matrix equations forms [35], [36]:

$$T_{6 \times 1} = c_{6 \times 6}^E S_{6 \times 1} - e_{6 \times 3} E_{3 \times 1} \quad (1.6)$$

$$D_{3 \times 1} = \varepsilon_{3 \times 3}^S E_{3 \times 1} + e_{3 \times 6} S_{6 \times 1} \quad (1.7)$$

Now the wave equation (1.5) has a three-dimensional character and is normally referred to as Christoffel's equation. The description of this equation and its solutions can be found in more detail elsewhere [35], [36]. For the sake of brevity, only the meaning of its solutions are included here. In an isotropic medium, this equation involves an eigenvalue problem whose eigenvalues are three real positive numbers corresponding to the three phase velocities of the possible propagating waves (one longitudinal and two shear waves, a fast-shear and a slow-shear, with polarizations normal to the propagation direction), and three eigenvectors defining the particle velocity directions or acoustic polarizations. In general, for a specified propagation direction, there exist three independent acoustic waves with polarizations mutually orthogonal. All acoustic modes that can be found in a solid are formed by one or a combination of these basic modes.

It is worth noting that, in an isotropic medium, these three basic modes are pure. However, in anisotropic media, like piezoelectric materials, the properties of these waves depend on the propagation direction and/or polarization, and the acoustic wave velocity. Therefore, pure longitudinal and pure shear waves are rarely found. They become quasi-longitudinal and quasi-shear with polarizations almost parallel and perpendicular to the propagation direction, respectively. Pure modes exist only for some specific symmetries [27], [36].

1.1.3. Types of electroacoustic devices

Normally EA devices receive their name attending to the type of acoustic wave they exploit. This depends on the excitation method, the device configuration, and the properties of the piezoelectric material. In this context, we can differentiate three main types of EA devices [20]:

- Bulk acoustic wave (BAW) devices [28], based on waves propagating through the volume, or bulk, of a piezoelectric material.
- Surface acoustic wave (SAW) devices [25], based on waves travelling, guided or unguided, across a stress-free single surface of a semi-infinite medium (substrate thickness $> 10\lambda$) [35].
- Acoustic plate mode (APM) devices [39], [40], based on waves travelling guided in plates, or membranes, of thicknesses comparable to their λ or thinner [35]. Since the acoustic waves are confined between both surfaces of the membrane due to multiple reflections, that is, they travel through the entire plate volume, they are sometimes classified as BAWs. Alternatively, they are sometimes considered SAWs [41] owing to the facts that they can be thought of as a combination of SAWs on both surfaces, and that most of them are generated using the same principles as in SAWs. In the APM category we can also include a specific type of devices that generate mechanical waves in piezoelectric plates, namely contour mode devices [42].

BAW resonators use a couple of metallic electrodes placed on both surfaces of a piezoelectric material, referred to as thickness mode excitation (Fig. 1.1). By applying an alternate voltage to these electrodes, BAWs can be generated and propagate through the volume of the piezoelectric substrate as transverse (shear) or compressional (longitudinal) waves. The resonant frequency in these type of devices is mainly determined by the thickness of the piezoelectric material (Eq. 1.1). The most traditional BAW-based resonator is the QCR, also known as thickness shear mode (TSM) resonator, employing the AT-cut quartz piezoelectric crystal (Fig. 1.1). The resonant frequency of TSMs is usually below 100 MHz (fundamental mode) [43], [44]. Their limitation in frequency stems from the fact that the physical thinning of the crystal has reached its limits [28].

To overcome this problem devices based on thin piezoelectric films can be used (Section 1.1.4) [31], [38].

The excitation mechanism of SAWs, and most of APMs, is based on several metallic strips placed on the top surface of a piezoelectric material forming an interleaved alternating pattern, referred to as interdigital transducer (IDT) (Fig. 1.2) [27][45]. These spatially periodic electrodes generate a SAW or APM, which propagates across a surface, or within the volume of a thin plate, respectively. SAW-based devices (including APMs) can be found in two configurations, as one or two-port resonators (Fig. 1.2a) [46], or as two-port delay lines (Fig. 1.2b) [47]. In the first case, the acoustic energy is confined in a resonant cavity formed (e.g. by two reflector gratings placed at both sides of the IDT). One-port resonators use a single IDT for excitation and read-out, while two-port resonators use two IDTs, one for the wave generation and the other (very close to the first one) for the readout. The operating frequency in this type of resonators is mainly determined by the IDT and reflectors periods (λ_{IDT} and λ_{REF} , respectively), the width of the cavity and the acoustic velocity in the substrate. (Fig. 1.2a). Typical strips dimensions are $\lambda/4$ long in the wave propagation direction and much wider than λ in the width direction. Regarding the delay line configuration, an input IDT is used to launch the wave and a second IDT is used for its collection after it has travelled a distance across the surface. In this case no reflectors are included, since the aim here is not to confine the acoustic wave in a cavity but to monitor the acoustic wave characteristic after a delay of finite time. The advantages and disadvantages of resonators and delay lines in sensing applications are discussed in Section 1.3. Typical piezoelectric substrates for SAW-based devices are also single crystalline materials like ST-cut quartz, LiTaO_3 or LiNbO_3 [27]. Their operating frequency when using these materials is below 1 GHz. Limitations in frequency come, in this case, from the lowest achievable IDT finger separation, imposed by the available optical methods in the semiconductor industry, or the acoustic velocity of the bulk single crystal piezoelectric materials. One of the solutions is the use of thin piezoelectric films with high acoustic velocities (Section 1.1.4).

Fig. 1.2. Sketch of the top and side views of a SAW-based resonator (a) and a delay line configuration (b). The orange arrow indicates the wave propagation direction.

A simplified summary of the main characteristic acoustic modes in EA devices, commonly used in sensing applications, is given in Table 1.1. As mentioned, basically all acoustic modes can be defined as a composition of the three fundamental acoustic wave solutions (Section 1.1.2.). For a better understanding of SAWs and APMs, the wave polarization with respect to the substrate surface, which defines the particle motion, should be considered before [27], [48]. Fig. 1.3 presents the three simple polarization schemes; their combination gives rise to elliptical polarizations as observed in Table 1.1.

Fig. 1.3. Scheme of the fundamental acoustic waves polarizations. Black arrows represent the particle displacement and the orange arrow the propagation direction. Longitudinal (L) (a) and shear (S) (b) are the basic polarizations for bulk modes. Shear horizontal (SH) (c1) and shear vertical (SV) (c2) are particular cases of the transverse polarization considering the surface particle displacement [27], [48]

TABLE 1.1 Summary of characteristic acoustic wave modes [28], [35], [48], [49]

ACOUSTIC WAVE		DESCRIPTION
Bulk Acoustic Wave (BAW)	Longitudinal (L)	<i>Polarization parallel to the propagation direction. (Thickness mode)</i>
	Shear (S)	<i>Polarization parallel to the substrate surface and perpendicular to the propagation direction. (Thickness mode)</i>
Surface Acoustic Wave (SAW)	Rayleigh-SAW	<i>Guided along the surface with elliptical polarization (combination of L and SV) with dominant component perpendicular to the surface.</i>
	SH-SAW	<i>Waves with polarization parallel to the substrate surface. (SH)</i>
	Leaky-SAW	<i>SAW with mainly SH component but not pure. Not completely confined near the surface but leaking energy to the substrate through the small SV component.</i>
	Love waves ¹	<i>SH-SAW guided along the surface when a continuous solid layer with slow shear velocity is deposited on the substrate.</i>
	Surface Transverse Waves (STW) ¹	<i>SH-SAW guided along the surface by metal gratings.</i>
Acoustic Plate Mode (APM)	SH-APM	<i>Guided SH waves travelling across both surfaces of plates with thickness of few λ.</i>
	Lamb waves	<i>Guided waves, in plates with thicknesses smaller than λ, composed of L and SV. They have elliptical polarization with displacements in both the propagation direction and perpendicular to the plate surfaces.</i>

¹ They can be considered surface skimming bulk waves trapped to the surface by a slowing physical effect — solid layers, with lower shear velocities, for Love waves, and metal gratings, where planar resonance occurs for STW.

1.1.4. Thin film electroacoustic devices

As introduced, the new standards imposed to EA devices regarding higher operating frequencies, monolithic integration and miniaturization, among others, cannot be fulfilled by using bulk single crystalline piezoelectric materials. These materials have several drawbacks. In BAW devices technology, there is a lack of proper plate thinning techniques allowing to achieve frequencies in the GHz range. In the case of SAW-based devices, the problems arise owing to the low acoustic velocities of the substrates and the submicron metal patterning, which increases electro migration among the metallic strips at medium and high operating powers [50]. Thin film piezoelectric materials appeared as the potential solution for the imposed standards. One of the first concepts regarding the use of a thin piezoelectric film consisted on the evaporation of a CdS thin film on a bulk quartz crystal in 1967 [51]. Years later, advances in the microelectronics industry in terms of high-resolution lithographic processes and physical deposition methods, especially sputtering, opened up the way towards the thin film electroacoustic (TEA) technology. This gave rise to a new branch of BAW-based resonators, the thin film bulk acoustic wave resonators (FBARs) [31], [32], [52], which have overcome the operating frequencies limitations of QCRs by reaching several GHz. The first composite resonators using ZnO were presented in the early 1980s [53]–[55]. This achievement can be considered the precursor of the FBAR technology. Although widely used, ZnO is not the preferred choice nowadays since it displays increasing losses in the GHz range, presents chemical instabilities and does not offer the highest figure of merit ($k^2 \cdot Q$). Owing to its unique properties, AlN has become the most attractive material in FBARs [56]. It offers several advantages, such as high acoustic velocity, low acoustic losses at high frequencies, high thermal and chemical stability [57], and IC compatibility, although the latter has not yet been exploited [58]. All these features along with the maturity gained in its sputtering deposition process [59]–[62], have made AlN the only thin piezoelectric material used in commercially available devices [63]–[65]. The fast development of the thin film technology also boosted the fabrication of Lamb wave-based devices. Initially in delay lines configurations using PZT [66], or ZnO [40], and more recently in resonator configurations using AlN and operating in the GHz frequency range [67]–[71]. In SAW-based devices the pursuit of higher frequencies prompted the use of high velocity thin piezoelectric films [72], [73]. Moreover, advances in techniques like the high-resolution electron beam lithography have also benefited the fabrication of higher frequencies devices [50]. Nowadays SAW devices working at up to 10 GHz are manufactured using high velocity substrates, like diamond or sapphire films, in combination with ZnO or AlN and high-resolution lithographic processes [74]–[76].

This thesis deals with the most representative TEA devices: AlN-based FBARs and Lamb wave resonators (LWR). FBARs are the thin film analogous to QCRs. In this case a thin

piezoelectric film ($< 3 \mu\text{m}$) is sandwiched between two metallic electrodes (around one order of magnitude thinner than the piezoelectric film). Depending on how the acoustic isolation (i.e. the confinement of the acoustic energy in the resonant cavity) is performed, two types of FBARs exist: suspended FBARs [77] (Fig. 1.4a) and solidly mounted resonators (SMRs) [78](Fig. 1.4b). In suspended FBARs the isolation is achieved, as in QCRs, by the reflection at the electrode/air interface at both surfaces, while in SMRs the acoustic isolation is achieved by placing the electrodes/piezoelectric stack onto an acoustic reflector. This reflector is usually constructed in a symmetrical form by alternating high and low acoustic impedance materials with a quarter wavelength ($\lambda/4$) thickness. This structure is similar to optical Bragg mirrors but, in this case, the refractive index is substituted by the acoustic impedance. The acoustic impedance of a material is defined as the product of the sound velocity in the material and its mass density. It represents the opposition to the sound propagation through the material. Two types of acoustic thickness modes can be excited in both suspended FBARs and SMRs: longitudinal and shear modes. To excite the first one, the AlN needs to be deposited in a highly oriented c -axis form [59]. As for the shear mode excitation, normal excitation of piezoelectric materials grown with tilted grains has proven to be the most efficient way [79]–[81]. Despite the maturity of the deposition techniques of AlN, only the c -oriented deposition process has been industrialized. Thereby, only FBARs using the longitudinal mode are commercially available. Although high quality tilted AlN films, and hence high-performance shear mode FBARs have been obtained in laboratories, the extension of the tilted grains deposition process to industry is still facing the lack of thickness uniformity drawback.

Fig. 1.4. Transversal scheme of a suspended FBAR (a) and an SMR (b).

LWRs belong to the acoustic plate mode (APM) family (Table 1.1), thus are based on membranes. Compared to the other main type of devices composing the APM family – shear horizontal-APM (SH-APM) devices – Lamb wave devices are generated in membranes with thicknesses of the order of λ or thinner, thus the use of thin piezoelectric films is required. Their excitation mechanism is the one described for SAW-based devices (i.e. by means of an IDT). As in FBARs, LWRs can be fabricated with two configurations, attending to their acoustic isolation mechanism, that is, with reflector gratings [82] (Fig. 1.5a) or by edge reflection, also referred to as contour mode resonators [71] (Fig. 1.5b). Depending on the plate thickness to λ ratio, the plate can support a number of Lamb wave modes, each one consisting of two different families: symmetric and antisymmetric [22], [83] (Fig. 1.5c), indicating the symmetry of the particle displacement relative to the median plane of the plate. The different modes are denoted as S_n and A_n , for the symmetric and antisymmetric modes, respectively, where $n = 0, 1, 2, 3$, etc. indicates the mode order. Sometimes in the literature these two families are called extensional (S_n) or flexural (A_n) modes. Devices using the A_n modes are commonly referred to as flexural plate wave (FPW) devices [20]. Particularly the zero-order modes (S_0 and A_0) deserve special attention since they are the only ones existing over the entire frequency spectrum (they do not exhibit cut-off frequencies at zero lateral wavenumber), have low dispersion and high phase velocities [22].

Fig. 1.5. Transversal scheme of a grating type (employing reflectors) LWR (a) and an edge type (contour mode) LWR (b). Membrane deformation and particle displacement of the A_0 mode (c top) and S_0 mode (c bottom) [22].

1.2. Figures of merit of sensors

In general the performance of a sensor can be classified attending to characteristics such as sensitivity, selectivity, resolution, detection dynamic range, limit of detection, speed of response, recovery time, or stability [20], [84]. In the particular case of the EA resonators studied in this thesis, it is important to consider also some specific parameters that define the performance of the resonator. These are the effective electromechanical coupling coefficient of the device (k_{eff}^2) and its quality factor Q . As the intrinsic k^2 of the piezoelectric material (Eq. 1.4), k_{eff}^2 indicates how efficiently the electrical energy is transformed to mechanical energy, but in this case considering the complete device configuration. The quality factor Q , which quantifies the losses of the resonator, can be defined as the ratio between the stored energy in the oscillating resonator and the energy dissipated per cycle by damping processes [36]. Their detailed description, together with some fundamentals of EA resonators, is performed in Chapter 2. The other important sensor parameters are the following [85]:

- ◆ **Sensitivity (S):** the ratio of the magnitude of the sensor response to the magnitude of the quantity measured (measurand, M) [86]. In the case of EA resonators, the shift in their resonant frequency (Δf) when measuring a certain magnitude (ΔM), which can be external physical quantities like mass or viscosity. It is of common practice to consider S simply as the ratio of Δf and ΔM . However, if a comparison between sensors is pursued, the scale of S with frequency suggests the use of a normalized expression in order to reduce the sensitivity to frequency scaling [84]:

$$S_N = \frac{\Delta f}{f_0} \frac{1}{\Delta M} \quad (1.8)$$

where f_0 is the initial resonant frequency when no ΔM occurs.

- ◆ **Specificity or selectivity:** the ability to detect only the targets under interest without generating false positives.
- ◆ **Limit of detection:** is the smallest measurable input (measurand) in the presence of noise. It can be represented as the normalized smallest detectable change in the measured signal:

$$LOD = \frac{\Delta f_{min}}{f_0} \quad (1.9)$$

which can also be estimated as three times the noise floor ($\sigma_y(\tau)_{\min}$) [84]. It differs from the resolution, which is the smallest measurable change in the input.

- ◆ **Resolution (R)**: the minimum change in the measurand $\Delta M_{\min}$ that can be detected in the output signal. The most common technique to read or detect the output signal (i.e. value of the resonant frequency) is through a circuit based on an oscillating loop with the resonator in the feedback branch. It is then of crucial importance to consider the noise present in this oscillating circuit, since it directly affects the accuracy with which we are able to measure the resonant frequency. Therefore the resolution, being directly related to the noise present in the system, can be determined as [85]:

$$R = \Delta M_{\min} = \frac{LOD}{S_N} = \frac{3 \sigma_y(\tau)_{\min}}{S_N} \quad (1.10)$$

At the same time, the smallest amount of noise generated by an oscillator in vacuum, namely $\sigma_y(\tau)_{\min}$, can be determined as the empirical ratio between a constant ($1 \cdot 10^{-7}$) and the quality factor of the resonator (Q) [86]. This constant arises from the IEEE standard 1139-1988 for frequency stability measurement described in terms of the Allan deviation [87]. We can take then as a good approximation for the resolution factor (R_F), the following relation:

$$R_F = \frac{3 \cdot 10^{-7}}{Q \cdot S_N} \quad (1.11)$$

which indicates that the higher the $Q \cdot S_N$ product the lower the R_F . However, high $Q \cdot S_N$ products can be obtained with very high S_N and low Q , and vice versa. Therefore a trade-off between Q and S should be considered.

1.3. State of the art in electroacoustic sensors

Broadly speaking, sensors can be classified attending to the type of target, or measurand they are meant to detect. The types of measurands can be classified into:

- ◆ Physical (e.g. temperature, pressure, mass, density, viscosity)
- ◆ Chemical (e.g. vapors or gases, molecules in liquid solution)
- ◆ Biological (e.g. organic molecules such as proteins, DNA chains, bacteria, viruses, etc.)

Besides the target type classification, it is important to distinguish between the media in which the sensors have to operate, which have a significant impact on the selection of the operating principles of the sensor. In this context, they can be classified as sensors working in liquid media or in gaseous media (including air and vacuum). Both media can be additionally extended to more specific environments, like the corrosive or high temperatures ones (harsh environments). Physical and chemical sensors can be found in both, liquid and gaseous media, however biological sensors must generally operate in liquid environments since biological agents need a buffer solution for their existence [15], [88], [89]. An exception can be electronic noses, which perform breath analysis [8], [90].

1.3.1. Gaseous environments

All EA devices are operable in gaseous media [91]. Their most common application is as mass detectors (gravimetric sensors) in which a shift in their resonant frequency occurs when a specific mass is attached to their surface. QCRs, in this case also referred to as quartz crystal microbalances (QCMs), are the very first and most commercialized type of gravimetric sensors [24], [92]. Their first application was as film thickness detectors in evaporation systems [29], but their use was subsequently extended to chemical sensing applications [44], [93]. Their operating principle is based, in this case, on the mechanical perturbation the deposited mass produces on the resonator. That is, the added mass at the surface of the resonator (where the displacement is maximum, antinode) is equivalent to increasing the thickness of the device, which increases λ and lowers the resonant frequency [22]. This leads to the basic mass sensitivity defined by Sauerbrey [29], which infers that the mass sensitivity scales with the squared frequency. However, the use of this theory, which is the most generalized one, is only valid if the added film is thin enough so that the mass is effectively deposited at the antinode and the mechanical properties of the film are similar to the quartz ones [22]. There are more complete theories yielding similar expressions for the sensitivity, but with treatments that bring more physical insights. One is based on an acoustical approach [94]. It considers characteristic impedances, transmissions and reflections at the quartz/deposited film interface, and states that the wave must propagate in the deposited film for a frequency shift to occur. The other is a universal approach based on the Rayleigh principle that considers kinetic and potential energies interchanged by the system [22]. Other typical approach is based on the perturbation theory [95].

Due to the physical limitation of QCMs in terms of operating frequency and hence sensitivity, SAW-based devices, widely used in filters for the telecom industry, appeared as the alternative high-sensitivity devices [96]–[98]. The claim of their higher sensitivity is based on the increased concentration of acoustic energy in the near surface region, while in QCMs this energy is

distributed within the entire piezoelectric substrate. This, in turn, means that SAWs are more affected by the variations in the contacting medium. Particularly, Rayleigh-SAWs in delay line structures, using ST-cut quartz or LiNbO_3 , have been used as chemical sensors [98]–[101]. Love wave-based or surface transverse waves (STW) devices are more frequently applied in liquid environments, however they have also been used in gaseous media as mass detectors [102]–[105]. In this case the mass attachment is monitored by the variation in the phase and amplitude of the guided wave [22]. Although not as common as SAW delay lines, SAW resonators have been also employed as gas sensors [106], [107]. It is probably worth at this point to discuss which of these two configurations of SAW-based devices can be considered better. Delay line configurations have been thoroughly used owing to the information the travelling wave can provide when interacting with the adjacent medium. These are not only mechanical interactions, as in the QCM case, but also acoustoelectric, which vary the phase and amplitude of the travelling wave [22], [108]. However, in a delay line configuration the IDTs placed at both ends of the piezoelectric substrate surface generate waves that travel away from them in both directions. The ones travelling towards the ends of the substrate are lost, which leads to lower Q devices. In contrast, SAW-based resonators (in their one or two-ports configurations) trap the acoustic energy by the passive reflectors set at the sides of the IDTs [107], giving rise to higher Q devices more appropriate for the oscillating circuits typically used to exploit EA devices. In summary, resonator configurations are preferred owing to their higher Q , which provides sharper peaks easy to monitor, low insertion loss, and higher frequency stability [23].

As it occurred in the telecom industry with EA filters, one of the turning points in the sensing applications of EA devices was the development of thin piezoelectric films [109]. As previously discussed, piezoelectric thin films overcome the problems of bulk crystalline substrates by offering higher operation frequencies (thus higher sensitivities according to Sauerbrey's equation), higher velocities, and possibility of miniaturization and array integration. The most representative example of TEA devices in gas sensing applications are FBARs working in the longitudinal mode, initially using ZnO [110] and more recently AlN [111], [112]. These new devices operating in the GHz frequency range are boosting the gravimetric sensing performances. The development of the thin film technology also made possible the fabrication and application of Lamb wave devices to gravimetric sensors. Initially they were exploited in delay line configurations [113], and more recently very high mass sensitivities were proved with AlN -based LWR [85].

One method to improve selectivity in gas sensing applications is to coat the EA device with an active or absorbing layer, which can easily trap specific gas molecules and hence produce a variation in the response of the sensor [100]. The process of surface manipulation or conditioning

for selective sensing is known as functionalization. There exist a wide variety of materials and structures than can be used as coating films, being the most typical ones porous materials like polymers [114] and nanostructured materials [115]–[118]. Among the latter, carbon nanotubes (CNT) appear as the most attractive. They are 1D tubular structures formed from carbon honeycomb networks with diameters ranging from 1 nm to several nm [119]. Owing to their high surface to volume ratio and their high chemical compatibility with different functional groups [120], they can provide the sensor with increased functional area, rapid response and higher selectivity [121]. CNTs have been used in EA devices as dispersed thin coating films [117], [118], [122]–[124].

1.3.2. Liquid environments

While all EA devices can operate in gaseous media, the operation in liquid environments deserves special attention since it is restricted to only few of them [125]. An EA device can be suitable for in-liquid operation only if its acoustic wave mode does not suffer from prohibitive attenuation when contacting the liquid. That is, the acoustic wave does not couple to the liquid, hence acoustic energy radiation does not occur and Q degradation is avoided. Two conditions can fulfill the non-radiating requirement: 1) the acoustic waves should not have a surface normal component in order to avoid coupling to compressional waves in the liquid, and 2) if they have a surface normal component, the velocity of the wave should be lower than the velocity of the compressional waves in liquid [20], [125]. In this context, longitudinal-BAW devices and Rayleigh-SAW devices are unsuitable for in-liquid applications as they have a strong surface normal component and their performance is almost completely degraded in contact with liquids [20], [41]. Therefore the appropriate choice for in-liquid operation are shear mode-BAW devices, SH-SAW devices and APM devices [20], [125]. A vast variety of studies exist on their application either as physical liquid monitoring sensors or as gravimetric biosensors. As in gas sensing applications, QCMs were the first devices to be used in liquid phase [126] [127], followed by the different variations of SH-SAW-based devices like the ones based in Love waves [23], [128]–[130], STWs and leaky waves [23], [88], [131]. The latter claiming higher sensitivities again owing to their higher energy concentration at the top surface. SH-APM appeared also as a high sensitive choice for in-liquid applications [20], [23], [39]. Finally, TEA devices like shear-FBARs and Lamb wave-based devices have attracted attention owing to their increased mass sensitivities, potential for in-liquid operation, and the possibilities the thin film technology offers. Particularly, suspended-FBARs and SMRs employing ZnO and AlN with tilted grains have been extensively studied for biosensing applications [89], [132]–[134]. Additionally, Lamb wave devices have been commonly exploited in liquid environments using delay line configurations and the A_0 mode [113], [135], [136]. This mode has a strong normal component (Fig. 1.5c); however, if the plate

thickness to λ ratio is set small enough, the velocity of the wave can be lower than the sound velocity in the liquid, being the acoustic energy trapped within the plate [22]. Although the A_0 mode has been the most exploited one for liquid environments, the S_0 mode can also be a good candidate [137]. In contrast to the A_0 mode, it has a stronger extensional component compared to the normal one (Fig. 1.5c), which indicates similar sensing principles as in shear mode devices. The potential of the S_0 mode for in-liquid sensing has been proven only recently [69], [138].

1.3.3. Harsh environments

Lately, there is an increasing demand of sensors capable of operating in hostile or harsh environments, such as those found in the aerospace or industrial sectors. More particularly EA devices are requested to operate in environments where corrosion and very high temperatures ($>600^\circ\text{C}$) play a crucial role. This field is almost completely monopolized by SAW-based devices. Their ease of fabrication and potential for wireless interrogation have placed them as the preferred choice. Their application in such extreme conditions has required extensive studies on the proper material choice, either for the piezoelectric substrate or the IDTs. In the first case, LGS and its different alloys, appear as the most suitable owing to the high melting point of LGS [139]–[141]. LGS-based SAW have proven operability above 800°C and up to 1100°C [141], [142]. More recently, AlN (combined with sapphire) has also been investigated as a promising candidate for high temperature SAW devices up to 1000°C . LGS has certain drawbacks, such as a fast increase of propagation losses with frequency and temperature [143], which can be overcome by the use of AlN. However, although AlN is chemically stable and retains its piezoelectricity at even 1000°C , it is still not the strongest competitor owing to its poor oxidation resistance above 700°C [76], [144]. As for the metallic strips composing the IDTs, extreme caution has to be taken since the long, narrow and thin metallic strips are subjected to destructive agglomeration or de-wetting [145]. One of the most studied materials for IDTs is Pt and its different alloys [146], [147]. Ir in different alloys has also been proposed as a good candidate [76].

Few examples can be found in the literature regarding the application of other EA devices, particularly TEA devices, in harsh environments. These are related to AlN based-LWRs working at 600°C [148], and AlN-based FBARs (in this case SMRs) sustaining 250°C [149].

1.4. Objectives and organization of the thesis

The final goal of this thesis is to contribute to widen the knowledge in the field of TEA sensors by expanding and improving the physical and chemical applications of FBARs and LWRs. On one hand, S_0 mode LWR (S_0 -LWRs) are relatively new devices and, although their mass sensing (gravimetric) performance has been already studied, their sensing mechanisms in liquid

environments have not been fully explored yet. Compared to FBARs that use tilted-grain AlN films for their operation in liquid, S_0 -LWRs use *c*-oriented AlN. In this case the deposition process is already industrialized, which places them as the most promising candidates to be commercialized as in-liquid TEA sensors. This thesis theoretically and experimentally describes the in-liquid performance of AlN-based S_0 -LWRs and compares it to the widely studied shear mode FBARs one. A framework describing the in-liquid sensing performance of S_0 -LWRs can be useful not only for their application as physical sensors (e.g. density and viscosity monitoring), but also for discriminating the influence from the surrounding liquid in biosensing applications, where the main scope is to monitor mass attachment of measurands existing in aqueous solutions.

On the other hand, FBARs are relatively mature devices that have been thoroughly investigated in both gaseous and liquid environments. However, much efforts have been put on the latter leaving their gas sensing potential with unexplored possibilities. This thesis studies the improvement of AlN-based SMRs gas sensing performance by fully integrating CNT forests as active sensing layers. Vertically aligned CNTs (forest) are expected to improve selectivity and increase the surface area for target binding that other typical sensing layers like SiO_2 , Au or polymers offer. The direct integration of CNT forests on SMRs has two main requirements that are not straightforward: 1) the devices must withstand the high temperatures needed for CNT formation and 2) the CNTs must be capable of growing over the metallic top electrodes of the devices. Thereby, in this thesis special emphasis is put on the development of SMRs for high temperatures processing and the growth of CNTs on metallic substrates, which is still a pending matter in the CNT community. Additionally, SMRs operating in high temperature environments could be also placed as a promising alternative to the widely used SAW devices.

The thesis is organized in six chapters. The present chapter has introduced the working principles of EA devices and their application as sensors. The different types of EA devices have also been described as well as the state of the art in particular sensing applications.

Chapter 2 describes the fundamentals of EA resonators and the theoretical models employed for their simulation and analysis. These include the Mason's model and the finite element analysis method.

Chapter 3 summarizes the experimental techniques used for the fabrication and characterization of the devices. A detailed fabrication route of each device is included, together with a description of the measurements set-ups for their sensing applications.

Chapter 4 is devoted to the finite element modelling of AlN-based S_0 -LWRs and their behavior in contact with liquids of varying density, viscosity and dielectric permittivity. The established

model is verified through experimental results. At the end a comparison between the widely studied shear mode FBARs and the S_0 -LWRs is reported in view of their performance in liquid media.

Chapter 5 includes the investigations related to the operability of AlN-based SMRs at very high temperatures, and the full integration of CNT forest on their top electrodes for gas sensing applications. The first part of the chapter is dedicated to the design of devices (particularly acoustic reflectors) sustaining high temperatures. This is promising for their potential use in high temperatures environments and is needed for the integration of the CNTs. The second part deals with this integration. It includes a deep study on the growth of CNTs on different substrates, particularly the metallic top electrodes used in the SMRs and the influence of such integration on the device performance. Finally, a proof of concept of the CNT-based SMRs vapors sensing abilities is presented.

Lastly, Chapter 6 presents the conclusions of the thesis and describes the suggested future lines of investigation.

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Chapter 2

Fundamentals and modelling of electroacoustic resonators

This chapter includes the fundamental theory of electroacoustic resonators and the models, or methods, used for the design and analysis of the devices in this thesis. These are the Butterworth Van Dyke's model, the Mason's model, and the finite element analysis.

A resonator is a system with, at least, one degree of freedom where energy can be stored and transferred between two forms. For instance, a mass attached to a spring with 1D movement has the energy in kinetic form (inertia of mass when moving) or in potential (elastic constant in the elongated spring) form. At the resonant frequency this transfer is more efficient and the amplitude of the representative magnitudes is much higher than for any other frequency. An interesting example of a resonant system is an electrical LC tank, where the energy can be stored electrically in the capacitor or magnetically in the inductance. In all cases, an additional phenomenon also takes place, the dissipation of energy (losses). It is of common practice to use electrical models that describe the behavior of non-electrical systems. In our case, electroacoustic (EA) resonators are elements included in electrical circuits, hence the practical way to represent their behavior is by equivalent circuits. A chronological review of the most important achievements in the electrical representation of EA resonators can be found in [1]. In 1914, S. Butterworth first used an equivalent electrical circuit to represent a mechanically vibrating system [2]. This was followed by K. S. Van Dyke, who in 1925 discovered that the same circuit also characterized the impedance behavior of a piezoelectric resonator [3]. W. P. Mason subsequently introduced, in the 1930s, acoustic transmission lines, mechanical ports, and piezoelectric transformers, thereby

extending the use of the circuit to the electromechanical conversion in devices of wide generality, including the use of resonators as sensors [4]. Butterworth-Van Dyke's (BVD) model is a general electrical representation based on simple discrete elements. It was initially applied to the basic plate resonator with thin electrodes (Fig. 1.1.), but can be extended to more sophisticated structures or other types of resonators. From the analysis of the BVD equivalent circuit the expression of the resonator impedance can be extracted in a convenient pole-zero form. However, at microwave frequencies this expression only approximately describes the resonator. For structures where the electrodes have a thickness comparable to that of the piezoelectric film, or are composed of several layers, e.g. thin film resonators, particularly solidly mounted resonators (SMRs), Mason's model appears as a more appropriate solution [5]–[7]. Hence the choice of this technique for the design and analysis of SMRs in this thesis. It uses a 1D transmission line concept to derive a complete equivalent circuit of the resonator based on each material property (density, elastic, dielectric and piezoelectric constants). In the case of SMRs, Mason's model incorporates the electrodes and the mirror layers by using the network theory approach. This model is useful when the acoustic wave in the device is a plane wave, however if we are dealing with 2D guided waves, like Lamb waves, or we want to study the interaction between the device and the adjacent medium, more powerful modelling tools must be employed. In this thesis, the interaction of Lamb wave resonators with liquids is simulated by the finite element method (FEM), which is a powerful numerical-analysis tool able to solve problems of systems where different physical phenomena are involved (piezoelectric, electrostatic, fluidic, thermal, etc.). It is based on the implementation of the equations which govern and couple the different physical domains of the system on a finite element calculation process.

The following descriptions of the BVD and Mason's models are extracted from more exhaustive and detailed works like [5], [8]; the descriptions included here are a summary.

2.1. Butterworth Van Dyke's model

The BVD circuitual model represents the simple plate resonator (see Fig. 2.1) as a capacitance C_0 (the one of the sandwiched piezoelectric far from resonance) in parallel with the series of a capacitance, an inductance and a resistance (C_m , L_m and R_m), called the motional arm, which models the effects of mechanical resonance on the total electrical impedance of the device (Fig. 2.1 right). This electrical representation arises from the mechanical-electrical equivalences with the equation of motion of forced oscillators (string attached to a mass with an applied external force) [8]. In Fig. 2.1 (left) M is the contribution of inertia (kinetic energy storage in the moving mass), k the contribution of elasticity (potential energy storage in the compressed spring) and η the contribution of viscosity (friction losses) [9]

Fig. 2.1. BVD equivalent circuit of a simple plate resonator.

A more realistic equivalence is given by the modified BVD model (mBVD) [10], shown in Fig. 2.2, which includes the parasitic components always present in actual resonators and the non-ideal insulating character of the piezoelectric material. The additional R_0 , R_s and L_s , represent the dielectric loss in the piezoelectric material, the electrical resistance of the electrodes (including contacting) and the inductance formed by the electrode layout, respectively.

Fig. 2.2. Modified BVD equivalent circuit including parasites and losses in the materials.

The BVD equivalent circuit describes the resonance/anti-resonance behavior shown by an EA resonator, formed by a combination of both series and parallel LC circuits. At resonance, the reactance of the motional arm equals zero, which means that almost all the current passes through this branch, limited only by R_s and R_m . It can be considered as a series resonance or short circuit, given that the impedance tends to zero. From the condition of zero reactance, the value of the resonant frequency results [5]:

$$f_r = \frac{1}{2\pi\sqrt{L_m C_m}} \quad (2.1)$$

At anti-resonance, the reactance of the loop formed by the motional and electrostatic branch equals zero, meaning that the current circulates around the loop formed by C_0 and the motional arm without leaving it. In this case, we can consider it as a parallel resonance or open circuit, since the impedance tends to infinite (actually, to the real part of the impedance related with R_0 and R_m). Now the condition of zero reactance leads to the following anti-resonance frequency [5]:

$$f_a = \frac{1}{2\pi} \sqrt{\frac{C_m + C_0}{L_m C_m C_0}} \quad (2.2)$$

Fig. 2.3 represents the typical electrical impedance characteristic of an EA resonator. We can see here the described behavior at resonance and anti-resonance and how the resonator tends to the simple capacitor behavior far from these two frequencies. In both cases – resonance and anti-resonance – the phase of the impedance suffers a shift from -90° to 90° and vice versa.

Fig. 2.3. Impedance vs. frequency characteristic of an EA resonator and its phase.

When designing or analyzing an EA resonator there are many parameters to be considered depending on the final application. However, two key parameters stand out as the most important when describing the performance of a resonator: the effective electromechanical coupling coefficient and the quality factor.

2.1.1. Effective electromechanical coupling coefficient (k_{eff}^2)

This parameter measures how efficiently the resonator transforms energy from electrical to mechanical, and vice versa. It differs from the electromechanical coupling coefficient defined for a piezoelectric material (Eq. 1.4) in that it measures such efficiency in the whole resonator structure, which includes the electrodes and other surrounding materials [5]. It can be defined in terms of the relative spacing between f_r and f_a . Although there are many definitions widely used [11], the most accurate is the one proposed by the IEEE standard on piezoelectricity [12]:

$$k_{eff}^2 = \frac{\pi}{2} \frac{f_r}{f_a} \frac{1}{\tan\left(\frac{\pi}{2} \frac{f_r}{f_a}\right)} \quad (2.3)$$

2.1.2. Quality factor (Q)

An ideal resonator would never lose energy and would vibrate indefinitely with the same intensity even if the external force leading it to resonance, is removed. Nevertheless, real resonators have always certain losses that need to be considered. As introduced in Chapter 1, the Q factor is a relative measure of the rate at which the resonator loses energy. Its formal definition is the ratio of the energy stored in the oscillating resonator to the energy dissipated per cycle by damping processes [5]:

$$Q = 2\pi \times \left(\frac{\text{Energy stored}}{\text{Energy dissipated per cycle}} \right) = 2\pi f_r \times \left(\frac{\text{Energy stored}}{\text{Power loss}} \right) \quad (2.4)$$

There are two traditional methods to extract the Q factor from the electrical characteristics of an EA resonator. The first one is based on the full width of Δf at half maximum level of the real part of the admittance or impedance curves:

$$Q_{r,a} = \frac{f_{r,a}}{(\Delta f)_{FWHM}} \quad (2.5)$$

where $f_{r,a}$ is the resonant or anti-resonant frequency. The second one is based on a derivative method using the steepness of the phase curves at resonant or anti-resonant frequencies (Fig. 2.3):

$$Q_{r,a} = \frac{f_{r,a}}{2} \left(\frac{d\varphi(Z)}{df} \right)_{f_{r,a}} \quad (2.6)$$

An approximation of the Q factors at resonance and anti-resonance can be also derived from the mBVD equivalent circuit (Fig. 2.2):

$$Q_r \approx 2\pi f_r \frac{L_m}{R_s + R_m} \quad (2.7)$$

$$Q_a \approx 2\pi f_a \frac{L_m}{R_0 + R_m} \quad (2.8)$$

From these two approximations we can extract that the Q factor at resonance is loaded by the series resistance introduced by the electrodes, while the Q factor at anti-resonance is influenced only by the internal losses. This is due to the fact that at resonance the impedance of the motional arm is reduced to R_m , making the total current to be maximum and mainly flowing through the motional arm (the influence of R_s is the greatest), while at anti-resonance it becomes almost an open circuit making the current to reach its minimum value and flowing only through C_0 , gaining R_0 a more pronounced effect (the influence of R_s is the lowest).

Finally, it is important to note why the Q factor should be as high as possible. In the particular case of gravimetric EA sensors, the information provided by the sensor lies on the shift of the resonant or anti-resonant frequencies. To accurately determine this frequency two methods are typically used. The first one consists in inserting the resonator in the feedback loop of an electronic oscillator. The phase or jitter noise of the oscillator is directly proportional to the Q factor as the engaging phase depends on the slope of its variation with frequency. The lower the Q factor is, the higher the frequency fluctuations are. This reduces the limit of detection of a sensor based on frequency shifts using an oscillator as electronic excitation. The second method to extract the frequency shift is by determining the maximum of the real part of the admittance (at resonant frequency) or impedance (at anti-resonant frequency) spectra. If the Q factor is low, the width of these magnitudes is large and the determination of the maximum is less accurate.

2.2. Mason's model

In Chapter 1 we introduced the one-dimensional equation of a propagating wave in a solid (Eq. 1.5), whose solution is a plane wave. To further understand the derivation of Mason's model, we should consider first the solution of the equation in a d -thick non-piezoelectric slab composed of a lossless, isotropic and free charge medium (sketched in Fig. 2.4), where lateral dimensions are considered infinite.

Fig. 2.4. Sketch of a d -thick non-piezoelectric slab with incident and reflected waves at the top and bottom interfaces.

Reformulating Eq. 1.5 in terms of the mechanical displacement u :

$$\frac{\partial^2 u}{\partial z^2} = \frac{\rho}{c} \frac{\partial^2 u}{\partial t^2} \quad (2.9)$$

we find that the solutions to this equation are an incident and a reflected wave, hence the possibility of representing the mechanical wave in the slab by its phasor notation as:

$$u(z) = (a e^{-jkz} + b e^{jkz}) \quad (2.10)$$

where $k = \omega/v_{\text{wave}}$ is the wavenumber (v_{wave} is the propagation velocity of the wave), $\omega = 2\pi f$ is the angular frequency, and a and b are the amplitudes of the incident and reflected waves, respectively. To obtain the particle velocities v_1 and v_2 at z_1 and z_2 , respectively, we can derive Eq. 2.10 ($v = \partial u / \partial t$). And by solving for coefficients a and b we get to:

$$j\omega a = \frac{v_1 e^{jkz_2} - v_2 e^{jkz_1}}{2j \sin kd} \quad (2.11)$$

$$j\omega b = \frac{v_2 e^{-jkz_1} - v_1 e^{-jkz_2}}{2j \sin kd} \quad (2.12)$$

The mechanical force at the boundaries can be calculated considering $F = -AT$, where A is the area and T the stress ($T = cS = c (\partial u / \partial z)$):

$$F = Ac \frac{\partial u}{\partial z} = jAck (a e^{-jkz} - b e^{jkz}) \quad (2.10)$$

and the definition of acoustic impedance for the mechanical wave:

$$Z = \frac{-T}{v} = \frac{-cS}{v} = \frac{-c \frac{\partial u}{\partial z}}{\frac{\partial u}{\partial t}} = \rho v_{wave} = \frac{ck}{\omega} \quad (2.11)$$

By substituting Eqs. 2.11 and 2.12 in Eq. 2.10, and keeping in mind Eq. 2.11, we get to the expression of the solution of the mechanical wave in the non-piezoelectric slab as a function of force, particle velocity and acoustic impedance:

$$F_1 = \frac{Z}{j\sin(kd)} [v_1 - v_2] + jZ \tan\left(\frac{kd}{2}\right) v_1 \quad (2.12)$$

$$F_2 = \frac{Z}{j\sin(kd)} [v_1 - v_2] - jZ \tan\left(\frac{kd}{2}\right) v_2 \quad (2.13)$$

If we consider an analogy between electrical voltage (V) and mechanical force (F), and between electrical current (I) and acoustic displacement velocity (v), we can then relate the equations with the classic T-impedance distributed equivalent network for a transmission line of length kd [13] (see Fig. 2.5), obtaining thus an equivalent electrical circuit for a propagating wave in a non-piezoelectric slab. This equivalent circuit can be treated as a quadrupole using an ABCD matrix:

$$\begin{pmatrix} F_2 \\ v_2 \end{pmatrix} = ABCD \begin{pmatrix} F_1 \\ v_1 \end{pmatrix} \quad (2.14)$$

which allows deriving the total impedance when several layers are connected in sequence, by multiplying the corresponding ABCD matrixes.

Fig. 2.5. Equivalent circuit of the wave propagation in a non-piezoelectric slab represented by the T -impedance transmission line network.

Moving now to the object of our study – the solution of the propagating wave in a piezoelectric slab –, we can follow a similar procedure. The piezoelectric slab, on which an alternate voltage is applied, is represented in Fig. 2.6 considering infinitesimally thin electrodes at the top and bottom interfaces.

Fig. 2.6. Sketch of a d -thick piezoelectric slab with infinitesimally thin electrodes at the top and bottom interfaces.

Although the procedure is similar, in this case the influence of the piezoelectric effect has to be taken into account. This is translated to a correction factor as we saw in Eqs. 1.2 and 1.3. Now we have $F = -AT$ with $T = c^E S - eE$. From Eq. 1.3 we can derive E :

$$E = \frac{D}{\epsilon^E S} - \frac{e}{\epsilon^E S} S \quad (2.15)$$

leading to:

$$T = (c^E + \frac{e^2}{\epsilon^S})S - \frac{e}{\epsilon^S}E = c^D S - \frac{e}{\epsilon^S}E \quad (2.16)$$

By considering also $I = j\omega DA$, Eqs. 2.12 and 2.13 are transformed to:

$$F_1 = \frac{Z}{j\sin(kd)}[v_1 - v_2] + jZ\tan\left(\frac{kd}{2}\right)v_1 + \frac{e}{j\omega\epsilon^S}I \quad (2.17)$$

$$F_2 = \frac{Z}{j\sin(kd)}[v_1 - v_2] - jZ\tan\left(\frac{kd}{2}\right)v_2 + \frac{e}{j\omega\epsilon^S}I \quad (2.18)$$

Additionally, the I-V characteristic can be calculated. The voltage drop in the slab can be derived by integrating the electric field (Eq. 2.15) between z_1 and z_2 :

$$V = \frac{d I}{\epsilon^S j\omega A} + \frac{e}{j\omega\epsilon^S}(v_1 - v_2) \quad (2.19)$$

And the current can be obtained considering again $I = j\omega DA$

$$I = j\omega C_0 + \frac{e}{\epsilon^S}C_0(v_1 - v_2) \quad (2.20)$$

being $C_0 = \epsilon^S A/d$ the static capacitance of the dielectric plate. The above derivations lead us to Mason's model, consisting in the equivalent electrical circuit shown in Fig. 2.7. This new representation is the same as in Fig. 2.5, but besides the acoustical ports, a third electrical port is included through a transformer, representing the additional term from the piezoelectric effect. Finally, Mason's model together with the ABCD matrix tool (Eq. 2.14) can readily derive the electrical impedance, at the I-V port, of a multilayer structure (like the SMR of Fig. 2.8), by cascading transmission line sections where each non-piezoelectric layer is represented by the equivalent circuit of Fig. 2.5, and the piezoelectric film by Mason's model of Fig. 2.7 [6]. F and v at each interface can be calculated by considering all materials properties, and added to the total mechanical loads at both acoustic ports of the piezoelectric layer, which in turn provides a final impedance of the device.

Fig. 2.7. Equivalent Mason's model represented by the T-impedance transmission line network with an additional electric port.

Fig. 2.8. Example of the equivalent circuit of an SMR based on cascade connection of the equivalent circuits of all layers, being the piezoelectric film represented by the three-port network Mason's model. The substrate and top air interface are represented by their equivalent acoustical impedances.

2.2.1. Electrical impedance derivation

Since we are interested in the electrical input impedance expression, we can follow the approach described by Lakin *et al.* [7], [14] for a composite resonator (piezoelectric slab and electrodes) to derive it. This approach leads to the same equivalent circuit, hence the view of Mason's model as a natural consequence of this analysis. By using the piezoelectric constitutive equations and assuming time harmonic and quasi-electrostatic conditions, the impedance of the composite resonator results as:

$$Z = \frac{1}{j\omega C_0} \left[1 - k_t^2 \frac{\tan\left(\frac{kd}{2}\right)}{\frac{kd}{2}} \cdot \frac{(z_t + z_b)\cos^2\left(\frac{kd}{2}\right) + j\sin(kd)}{(z_t + z_b)\cos(kd) + j(z_t z_b + 1)\sin(kd)} \right] \quad (2.21)$$

where z_t and z_b represent the top and bottom acoustic impedance loads normalized by the piezoelectric acoustic impedance, Z_p . Particularly, a piezoelectric resonator with infinitesimally thin electrodes (Fig. 2.6) would be characterized by Eq. 2.21 with $z_t = z_b = 0$. By expressing $\tan(kd/2)$ as an infinite sum of rational functions, we get to the simple BVD equivalent circuit (Fig. 2.1) around the fundamental mode [5], [6]. For the general case of Eq. 2.21 and by expanding with partial fraction analysis, the input impedance of a composite resonator results in:

$$Z = \frac{1}{j\omega C_0 + \frac{1}{\frac{-1}{j\omega C_0} + n^2 \left(-j \frac{Z_p}{\sin(kd)} + \frac{1}{jZ_p \tan\left(kd \frac{kd}{2}\right) + Z_t} + \frac{1}{jZ_p \tan\left(\frac{kd}{2}\right) + Z_b} \right)}} \quad (2.22)$$

equation which, by simple inspection, readily leads to the Mason's equivalent circuit described before (Fig. 2.7). The transformer term is represented now by $n^2 = kd / (k_t^2 \omega C_0 Z_p)$.

2.2.2. Reflector design

The most convenient way to design the acoustic reflector in SMRs is by using two fundamental equations from the network analysis [13]. The first is the expression of the reflection coefficient at materials discontinuities for plane wave propagation, e.g. interface between two adjacent layers with different acoustic impedances (see Fig. 2.9) given by:

$$\Gamma = \frac{Z_l - Z_0}{Z_l + Z_0} \quad (2.21)$$

where Z_0 is the characteristic impedance of the region of incident wave (1) and Z_l the load impedance of the material beyond interface (2). The second is the transmission line equation for the input impedance given by:

$$Z_{in} = Z_0 \left[\frac{Z_l + jZ_0 \tan \theta}{Z_0 + jZ_l \tan \theta} \right] \quad (2.22)$$

In this case, Z_{in} is the overall input impedance seen from the outside of section 1 (Fig 2.9) and θ the total phase across this section.

Fig. 2.9. Sketch of the interface between two materials with different acoustic impedances. The orange arrow represents the wave propagation direction. Z_{in} is the input impedance of the whole structure seen from the left side and Γ is the reflection coefficient at the interface.

In an SMR structure, the reflection at the whole reflector interface with the resonator must be as high as possible, i.e. $|\Gamma| \approx 1$, thereby the total input impedance of the reflector stack must be either much smaller or much larger than that of the piezoelectric material. This stack is composed of $\lambda/4$ -thick high and low impedance alternating layers for optimal reflection at a central frequency (f_c), being $\lambda = v_{wave} \cdot f_c$ the wavelength of the particular propagating mode needing to be reflected, and v_{wave} the velocity of the wave in the corresponding material of the stack. The total impedance at the reflector interface can be derived by recursive relations between the impedances of each layer, which reduces to $Z_{i,n} = Z_n^2 / Z_{i(n+1)}$. Here Z_i refers to the input impedance of section n . Multiple reflections from a number of layers adding in phase are used to achieve either an open $\Gamma = -1$ or clamped interface $\Gamma = 1$. Layers are added until sufficient reflection is achieved for a proper resonator response.

2.2 Mason's model

Typical materials used in acoustic reflectors as high impedance layers are high density metals, such as Ir, W or Mo, or insulating like AlN, Si₃N₄ or Ta₂O₅ [15]–[19] for fully dielectric reflectors, although the latter show significantly lower impedances. Regarding the low impedance layers, SiCO, AlN, Ti, or SiO₂ [20], [21] can be used, being the number of layers of the final structure dependent on the acoustic impedance mismatch between the two chosen materials. For this thesis the standard structure for SMRs is composed of the piezoelectric stack (AlN film sandwiched between an Ir bottom electrode and a Mo top electrode) and the acoustic reflector that alternates five layers of Mo and SiO₂. The latter was specifically designed for sustaining high temperatures (up to 700°C) when needed, as will be described in Chapter 5.

The most convenient way to characterize a reflector is by its logarithmic transmittance form:

$$T_{dB} = 10 \log_{10}(1 - |\Gamma|^2) \quad (2.23)$$

where Γ is the reflection coefficient, for acoustic power density, of the entire stack for a specific mode (longitudinal or shear).

In this thesis, the design and post-analysis of SMRs have been performed by implementing Mason's model in Matlab. Fig. 2.10 shows, as an example, the impedance response of a standard 2.5 GHz longitudinal mode SMR through the described cascading method, and the transmittance of its reflector. It consists of a 150 nm-thick Mo top electrode, a 1 μ m-thick AlN, a 120 nm-thick Ir bottom electrode, and an acoustic reflector of five alternating layers of 629 nm-thick Mo – 620nm-thick SiO₂. The response of the reflector for the shear mode is also included. For optimal performance of the latter, different thicknesses should be used.

Fig. 2.10. Electrical response of a designed 2.5 GHz SMR operating in the longitudinal mode with $Q_r = 800$, $Q_a = 900$ and $k_{\text{eff}}^2 = 6.5\%$. The black line represents the input impedance of the device computed using Mason's model together with the ABCD matrix tool, and the blue and red lines are the reflector transmittance values for the longitudinal and shear acoustic modes, respectively. To be noted that the reflector is specifically designed for full reflection of the longitudinal mode at 2.5 GHz.

2.3. Finite element analysis

FEM is a powerful tool able to accurately solve any problem governed by differential equations. The great advantage is that it can couple the different physical phenomena involved in a system (electrostatic, piezoelectric, thermal, optical, fluidic and electromagnetic, among others) by simultaneously considering their effects in the calculations. It allows solving structures in 1D, 2D and 3D. Due to the 2D nature of Lamb waves, a 2D model has been used in this thesis for modelling S_0 -LWRs and more particularly their interaction with adjacent liquids. A specific liquid model has been implemented to properly account for the energy viscous coupling to the liquid domain. This model will be discussed in more detail in the Chapter 4. For comparison purposes, FEM has also been used for modelling shear SMRs and suspended FBARs and their behavior in contact with liquids.

FEM is implemented and commercially available in several software forms (ANSYS, Coventor, COMSOL, etc). COMSOL 4.3b [22] is the one used in this thesis. To solve a problem by FEM analysis few steps need to be sequentially followed. For the particular case of EA resonators modelling, these are:

2.3 Finite element analysis

1. Choosing the piezoelectric devices interface, which combines the solid mechanics and electrostatic physics. The piezoelectric effect is modeled by solving the constitutive equations; the solid mechanics interface, based on solving Navier's equations, computes stresses, strains and displacements. The electrostatic interface computes electric field, electric displacement field and potential distributions by using Gauss' law.
2. Defining the geometry of the resonator of the system under study (e.g. resonator + contacting liquid).
3. Choosing the materials of the structure.
4. Setting the boundary and initial conditions of the system.
5. Meshing the structure by dividing it in a number of elements. In our particular case, the number of elements to be chosen is set by the minimum λ we need to solve in the structure. It is recommended to set a minimum of 10 elements per λ . The higher the number of elements, the less efficient the computation will be. A trade-off has to be reached.
6. Choosing a study type. In our case an initial eigenfrequency study is performed. Here no external forces are considered in the equations and natural resonating modes are computed. This study is useful for the initial evaluation of the structure. Subsequently the problem is deeply analyzed using the frequency domain study.
7. Solving. Equations are applied and solved for each element and superposed at the end for the global system evaluation.

Fig. 2.11 presents the 2D modelling of a 900 MHz S_0 -LWR by FEM. It shows a single λ unit cell (an IDT pair) consisting of 2 μm -thick AlN with two 270 nm-thick and 3 μm -width Al electrodes. Al electrodes are defined as linear elastic materials. Lateral continuous periodic conditions are applied, which avoid the presence of possible spurious modes generated from clamping the membrane on its sides. Fig. 2.12 plots, as an example, the simulated electrical response of the described structure.

Fig. 2.11. FEM 2D modelling of an AlN-based 900 MHz S_0 -LWR: (a) boundary conditions of the structure including lateral continuity, grounded bottom interface and voltage applied to the electrode, (b) meshing aspect of the structure, and (c) calculated displacement with deformation close to resonance.

Fig. 2.12. Modulus of the impedance and real part of admittance (conductance) spectra of the 900 MHz S_0 -LWR FEM simulation. It shows a $k_{eff}^2 = 0.5\%$ and a Q_r of 2000 (set by the losses in the AlN layer).

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Fabrication and characterization techniques

The complete device fabrication process as well as the characterization techniques, are presented in this chapter. These include fabrication methods like the sputtering and chemical vapor deposition (CVD), and techniques for materials characterization like the X-Ray diffraction or Raman and Fourier transform infrared transmission (FT-IR) spectroscopies. Additionally, the measurement set-ups configured for the different applications of the devices (in-liquid sensing, high temperature and gas sensing) are presented.

3.1. Fabrication techniques

Different deposition techniques have been used during this thesis. Controlling the parameters that govern the growth process is crucial for obtaining materials with the desired properties. Although a deep insight into the physics behind each technique is not undertaken in this section (related literature can be found elsewhere [1], [2]) a short description of the most important deposition systems is included.

3.1.1. Sputtering deposition

The physical sputtering process is based on the ejection of atoms from the surface of a target subjected to an energetic ion bombardment. The ions, typically extracted from a low pressure electrical glow discharge (plasma), erodes the surface of the target by extracting single atoms, which subsequently condense onto the substrate forming a film. In the case of reactive sputtering,

3. Fabrication and characterization techniques

a reactive gas is introduced in the plasma atmosphere, making it possible to grow compounds of the extracted atoms and the reactive gas atoms (for example oxides or nitrides by adding oxygen or nitrogen, respectively). Three reactive magnetron sputtering systems have been used in this thesis: two high vacuum (HV) systems for the deposition of the metallic electrodes and the different layers composing the reflectors (Ti, Mo, Ir, Cr, Ta, Al, W, SiO_x, SiO₂) and a custom-made ultra-high vacuum (UHV) system specifically designed for the growth of high quality piezoelectric AlN films. In all cases pulsed DC plasmas are used.

3.1.1.1. High vacuum systems

The two HV systems are implemented on single vacuum chambers pumped by a turbo molecular pump to the 10⁻⁶ -10⁻⁷ Torr range. Both use 99.99 % purity targets of different diameters. The system in which SiO₂, Ti, Mo, Ta and Al are deposited uses 15 cm in diameter targets, while the one used for Cr, Ir and Au deposition uses targets of 7.6 cm in diameter. In both cases the target to substrate distance is of 4.8 cm. Different targets can be used without breaking the vacuum conditions, allowing thus multilayer deposition. Substrate rotation and oscillation allow increased uniformity. Typical process parameters for the mentioned materials are presented in Table 3.1. Variation of these parameters for tuning material properties will be discussed in the corresponding chapters. Special attention will be devoted to adjustment of the deposition parameters for achieving low stress acoustic reflectors needed for the use of SMRs at high temperatures (either for high temperature applications or for the integration of CNT forests on their top electrode).

TABLE 3.1 Sputtering parameters of materials deposited in the HV system

Material	Power [W]	Ar [sccm]	O ₂ [sccm]	Butterfly valve	Pressure [mTorr]
porous-SiO ₂	1200	44	16.5	Yes	9.0
SiO ₂	1200	4.2	25	Yes	3.5
Ti	150	30	-	Yes	4.0
Mo	400	18	-	No	1.6
Ta	800	18	-	No	1.6
Al	700	30	-	No	3.0
Cr	500	30	-	No	3.0
Ir	200	30	-	No	3.0
Au	200	30	-	No	3.0

3.1.1.2. Ultra-high vacuum system: AlN growth

The second system is an ultra-high vacuum dual chamber one that deserves special attention. It is a custom-made system (Fig. 3.1) designed with the aim of controlling the optimal sputtering conditions that allow growing highly piezoelectric AlN films. The first chamber or transference chamber, intended for loading the samples, can be pumped to 10^{-6} - 10^{-7} Torr in a short time; the second chamber (deposition chamber), hardly ever vented, is maintained at ultra-high vacuum ($< 1 \times 10^{-8}$ Torr) by a cryogenic pump. AlN films are sputtered here from a 99.999 % Al target, 150 cm in diameter and located at a distance of 5.5 cm from the substrate. The latter is placed on an insulated substrate holder which allows RF biasing and heating. The reactive environment consist of 60% N_2 in Ar gas mixture.

Fig. 3.1. Dual-chamber ultra-high vacuum sputtering system for the deposition of AlN film.

Depending on the desired acoustic mode of operation, two types of AlN deposition processes have been employed. The first one, and most extensively used, has been developed for the growth of highly textured c -axis oriented films for longitudinal-SMRs and S_0 -LWRs. The second one is used for obtaining the tilted c -axis AlN films needed for the excitation of the shear mode in SMRs. These last were used for the specific comparison of their in-liquid behavior with the S_0 -LWRs one.

3.1 Fabrication techniques

For the growth of *c*-axis oriented AlN films the samples need to be placed on the center of the substrate holder (on-axis deposition). In the case of SMRs, AlN films were deposited on silicon samples containing acoustic reflectors, the uppermost layer of which was polished and covered with an evaporated Ir bottom electrode before AlN growth [3]. Polishing is essential to achieve highly oriented films, since AlN is strongly dependent on the texture and smoothness of the underlying layer [4]–[6]). For LWRs, AlN was grown directly on Si wafers. An Ar plasma cleaning, prior to the AlN deposition, was applied to the substrate in all cases. Typical process parameters for this type of growth are: a cathode power of 1200 W, a pressure of 1.6 mTorr, substrate biased at -65 V and heated to 400°C. Stress control of the AlN films is very important for SMRs supporting high temperatures and LWRs, where the AlN film is released to form a suspended membrane. In both cases, the AlN films should have null stress or slightly tensile stress [7], [8]. In this thesis the residual stress in AlN films has been controlled with the substrate RF bias [9], being -50 V the optimal value to achieve slightly tensile stress.

Tilted *c*-axis AlN films were deposited using a two-step process, which starts with the deposition of a 100 nm-thick AlN inactive (non-piezoelectric) seed layer grown under a low-energy sputter process at high pressure (5 mTorr) and low power (600 W), without substrate biasing or heating. This first step yield to microcrystalline AlN layers with mixed orientations. This was followed by an energetic sputter process at 1200 W and 1.6 mTorr by biasing the substrates at -65 V and heating them at 400°C. In this case, the samples were placed at the edge of the substrate holder, 5 cm far from the center (off-axis deposition). The combination of a microcrystalline seed layer and the off-axis deposition has been proved to be the best way for achieving AlN films with the *c*-axis tilted with respect to the surface normal [10], [11]. The characterization of both *c*-axis oriented and tilted AlN films is presented in Section 3.2.1.

3.1.2. Chemical vapor deposition for CNT growth

Among the different methods typically used for CNT growth [12], namely arc discharge, laser ablation and chemical vapor deposition (CVD), only the last one offers controlled growth and allows industrial production at low cost [12]–[14]. This has made it the preferred and most extensively studied method. The CVD method is a widely known technique typically used for thin films deposition. It is based on the thermal decomposition of gases in a reactor chamber where a certain temperature and pressure are established. In cold wall reactors, only the substrate is heated and a precursor gas flows into the chamber with the subsequent chemical reaction occurring near the substrate surface, which results in the film deposition [15].

This technique has been used in this thesis for the selective growth of CNT forests and their integration in SMRs. Particularly, the system used here is a thermal low pressure and cold wall CVD (see Fig. 3.2). The substrate holder is a pyrolytic carbon heater placed under a shower-like gas feeding. The temperature of the samples is controlled by means of a programmable temperature controller using the signal of a *K*-type thermocouple directly sit atop the sample. The chamber is pumped down by a rotatory pump to sub atmospheric pressures (10^{-4} Torr) and cleaned of oxygen by flowing high purity nitrogen in repeated vacuum-purging schemes before processing.

Fig. 3.2. Low pressure CVD system for CNT growth.

The CNT growth process is basically divided in two stages (Fig. 3.3): (1) formation of the catalytic nanoparticles (NPs) and (2) growth of CNTs. For the NPs formation, a very thin film (nm scaled thickness) of a suitable catalytic metal, typically Ni, Co or Fe [16], coalesces into small NPs under reducing atmosphere and high temperature conditions. The CNTs growth is promoted by flowing a light hydrocarbon gas which at high temperatures decomposes into H_2 and C species when coming in contact with the NPs. During this step, while H_2 flies away C dissolves into the NPs and when it reaches the carbon-solubility limit, it nucleates forming a tubular honeycomb C network [13], [17]. Depending on the strength of the NP-substrate interaction the growth can follow a base-growth model (interaction is strong and precipitation of C happens on top of the NP), or a tip-growth model (interaction is weak and precipitation of C occurs underneath the NP pushing it off the substrate) [13]. Fig. 3.3 illustrates these two growth models.

Fig. 3.3. CNT growth stages: (1) NPs formation and (2) CNT growth following a base or tip growth model.

Various reducing and precursor gases can be used in this process [13]. In this thesis NH_3 has been used as reducing gas and C_2H_2 as the precursor one. The types of gases, the type of catalytic NPs, and the substrate material are some factors that strongly affect the final structure of the CNTs. As it will be discussed in Chapter 5, controlling the material and process parameters are crucial for the synthesis of either SWCNTs or MWCNTs, with defined area density (tubes per unit area) and length.

3.1.3. Device fabrication routes

This section describes the processes followed for the manufacturing of standard devices, i.e. 900 MHz S_0 -LWRs and 2.5 GHz longitudinal SMRs. Specific modifications or routes extensions (e.g. CNT forests integration on SMRs) will be described in the corresponding chapters.

3.1.3.1. Lamb wave resonators

- Sputtering of 2 μm -thick c -oriented AlN with no stress, or slight tensile stress, on bare Si (100) wafer.

■ Al ■ Photoresist

- Sputtering of 270 nm-thick Al film. Deposition of photoresist and standard photolithographic patterning for IDT and reflectors definition.

- Dry etching of Al in BCl_3/Cl_2 plasma with subsequent O_2 plasma passivation of electrodes sidewalls. Removal of photoresist.

- Deposition and definition of backside Al hard mask by standard photolithographic process and Al etching.

- Photoresist removal and etching of Si substrate by a three-step Bosch process.

- Removal of Al hard mask¹.

- Top view of the device (optical image).

¹ In some cases a bottom 100nm-thick Mo electrode was sputtered through the Si cavity on the backside of the AlN membrane.

3.1.3.2. Solidly mounted resonators

- Sequential sputtering of five alternating layers of 629 nm-thick Mo and 620 nm-thick SiO₂ on bare Si (100)². Additional 15 nm-thick Ti layers between each Mo-SiO₂ layer for improving adherence. Mechanical polishing of the last SiO₂ layer using 0.05 μm grains alumina powder for optimal AlN growth.

- Sputtering of a thin 15 nm-thick Ti layer on the polished SiO₂ layer and e-beam evaporation of a 120 nm-thick Ir layer that will act as bottom electrode.

- Sputtering of 1 μm-thick *c*-oriented AlN following the deposition process described before.

- Sputtering of 150 nm-thick Mo film. Deposition of photoresist and standard photolithographic patterning. Wet Mo etching for top electrode definition.

²The structure of 900 MHz shear SMRs was the following: acoustic reflector composed of five 875 nm-thick porous-SiO₂/ 958 nm-thick Mo alternating layers, 160 nm-thick Ir bottom electrode, 1.6 μm-thick tilted AlN with previous 100 nm-thick seed layer, and 500 nm-thick Mo top electrode.

- Photoresist removal. Bottom electrode is contacted from the top side by capacitive coupling. On the right, top view of a real manufactured device.

- Top view of the device (optical image).

3.2. Characterization techniques

During this thesis different methods have been employed for assessing the structural characteristics of the materials and the overall performance of the devices. This section summarizes the structural characterization techniques of the key materials developed in this thesis, namely AlN, acoustic reflector layers and CNTs, and the electrical characterization of the final devices.

3.2.1. AlN characterization

The final performance of EA resonators is strongly dependent on the quality of the AlN film. In other words, a good device performance (high Q -factor and high k_{eff}^2) can only be achieved from high quality piezoelectric AlN (low material loss and high intrinsic k^2). In this thesis the crystal structure characterization of AlN films was tested by X-Ray diffraction measurements (XRD) and Fourier transform infrared spectroscopy (FT-IR). Overall device performance was assessed by regular scattering parameters analysis through network analyzer measurements. Owing to the importance of the AlN quality, only results regarding this material are presented in this section, however the techniques have been employed for other thin films as well.

3.2.1.1. X-Ray diffraction

Conventional θ - 2θ measurements and ψ scans were used to assess the crystal orientation of the deposited AlN films. Fig. 3.4 presents the θ - 2θ scan of a c -oriented AlN film grown on Ir electrode. High c -orientation is exhibited through high (00·2) peak and low presence and/or low intensity of non-(00·2) peaks [18], which indicates a majority of grains with orientation in the preferred growth direction (00·2). Inset of Fig. 3.4 presents the full width at half maximum (FWHM) of the (00·2) AlN rocking curve, which indicates the texture quality of the highly c -oriented AlN film. The value of the FWHM for the c -oriented AlN films deposited in this thesis are $\sim 1.2^\circ$, in agreement with the current state of the art in AlN sputtering deposition [18]–[21].

Fig. 3.4. XRD θ - 2θ pattern of a typical c -oriented AlN grown in this thesis. The inset presents the ψ scan of the rocking $\{00\cdot2\}$ curve.

In Fig. 3.5., the XRD pattern of a typical AlN film with tilted grains is shown. This type of films were the ones used in shear SMRs for their comparison with the in-liquid behavior of S_0 -LWRs. The intensity of the (00·2) peak is very low while the rest increase pointing to mixed orientations. Fig. 3.6 shows the pole figure of such a film. From this figure we can extract the tilt angles, with a mean angle around 30° .

Fig. 3.5. XRD θ - 2θ pattern of a typical tilted grains AlN grown in this thesis.

Fig. 3.6. XRD (00·2) pole figure of a typical tilted grains AlN grown in this thesis.

3.2.1.2. Fourier transform infrared spectroscopy (FT-IR)

As a simpler and faster alternative to XRD analysis, FT-IR measurements can be employed to assess the crystalline texture of AlN films. By analyzing the longitudinal optical (zone) through the $E_1(\text{LO})$ and $A_1(\text{LO})$ vibrational modes, the AlN grains orientation can be derived [22], [23]. Infrared reflectance spectra were measured in this thesis with non-polarized light at an incidence angle of 30° between 400 and 4000 cm^{-1} . Fig. 3.7 shows the reflectance spectrum (in absorbance units) of a c -oriented AlN film grown on Ir. The *reststrahlen* band – total reflection between the transverse optical (600 cm^{-1} – 700 cm^{-1}) and the longitudinal optical (850 cm^{-1} – 950 cm^{-1}) zones – is clearly observed, as well as the interference bands in the AlN film. Fig. 3.8 shows close views of the LO zone for both c -oriented and tilted AlN films. The presence of the single $A_1(\text{LO})$ peak at 887 cm^{-1} determines the pure c -axis orientation of the film (Fig. 3.8a) [22]. On the contrary, the composed peak indicates the presences of grains with tilted c -axis [23]. In this case, the spectrum corresponds to a sample with a tilt angle of $\sim 24^\circ$.

Fig. 3.7 FT-IR spectrum of a typical AlN film grown in this thesis.

Fig. 3.8. Close views of the $A_1(LO)$ peak for a) c -axis oriented and b) tilt grains AlN films.

3.2.1.3. Assessment of the film stress

The stress control in thin films has been of critical importance in this thesis. Particularly for the acoustic reflector layers, to avoid delamination when subjecting the SMRs at high temperatures, and for the AlN film, to avoid the mentioned delamination at high temperatures and the possible buckling or cracks when releasing the membranes in LWRs. The specific stress control of the layers composing the acoustic reflectors is described in Chapter 5.

A simple technique for the assessment of film stress is by measuring the bow of the films with an Inficon Dektak-150 stylus profilometer and deriving the stress through Stoney's equation [24], which relates the residual stress of a film (σ) deposited on a substrate to the variation of the curvature radius of the structure:

$$\sigma = \frac{E_s}{6(1 - \nu_s)} \frac{h_s^2}{h_f} \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (3.1)$$

where E_s , ν_s and h_s are the Young modulus, the Poisson ratio and the thickness of the substrate, respectively, h_f the thickness of the deposited film, and R and R_0 the curvature radii after and before the deposition of the film, respectively. Therefore, if the thickness, the elastic modulus and the curvature radius of the substrate are known, the residual stress of a deposited film, with known thickness, can be derived by measuring the curvature of the substrate after deposition.

3.2.2. Electrical characterization of resonators

AlN piezoelectricity and full performance of devices has been tested by measuring scattering parameters as a function of frequency [25]:

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \quad (3.2)$$

As our devices are one port resonators, only measurements of S_{11} were needed. These measurements have been performed with calibrated GSG RF-probes for on-wafer contacting, using an Agilent N5230A network analyzer (NA) (see Fig. 3.9). The complex S_{11} parameter can be readily translated to impedance values:

$$Z_{11} = Z_0 \frac{1 + S_{11}}{1 - S_{11}} \quad (3.3)$$

where $Z_0 = 50$ ohms corresponds to the system characteristic impedance.

Fig 3.9. Electrical characterization setup.

Figs. 3.10 and 3.11 show the logarithmic the impedance modulus and the real part of the admittance ($Y = 1/Z$) measurements of typical SMRs and S_0 -LWRs used in this thesis,

respectively. Admittance plots are represented by their real part, which are the monitored peaks in their sensing applications. On one hand the SMR is a 2.5 GHz longitudinal mode one and shows standard performance represented by $k_{eff}^2 = 6.85\%$, $Q_r = 420$ and $Q_a = 650$, which are in close agreement with the high quality of the AlN films and the current state of the art in devices with non-optimized acoustic reflectors [26]–[28]. On the other hand, the standard ~ 900 MHz S_0 -LWR without bottom electrode, presents a performance defined by $k_{eff}^2 = 0.6\%$ and $Q_r = 1400$, also in agreement with the state of the art if no optimization techniques are employed [8].

Fig. 3.10. Electrical response of a typical manufactured longitudinal mode SMR

Fig. 3.11. Electrical response of a typical manufactured S_0 -LWR.

3.2.3. CNT characterization

Different techniques can be employed for the characterization of the structure and hence physical properties of CNTs. In this thesis three methods have been systematically used for the assessment of the catalytic NPs size and distribution, the thicknesses of the CNT forests, and the tubes structural characterization. These methods are the atomic force microscopy (AFM), scanning electron microscopy (SEM) and Raman spectroscopy, respectively. From these, the latter deserves special attention since is one of the most powerful and widely used techniques for CNTs structural characterization.

3.2.3.1. Atomic force microscopy

To observe the size and distribution of the catalytic NPs, AFM measurements were performed on samples after the first stage in the process (see Fig. 3.3), just before the CNTs growth. The apparatus used is a Molecular Imaging Pico-LE working either in contact or tapping mode. In Fig. 3.12 an example of formed Fe NPs is shown.

Fig. 3.12. AFM image of catalytic nanoparticles formed from Fe.

3.2.3.2. Scanning electron microscopy

SEM observations were employed to assess the thicknesses of the CNT forests. The system used more often is a Karl-Zeiss DM995 microscope. In Fig. 3.13 a typical cross section image of a CNT forest grown on AlN is presented.

Fig. 3.13. Cross section SEM image of a CNT forest grown on AlN.

3.2.3.3. Raman spectroscopy

Raman spectroscopy is a fast, easy-to-use and non-destructive characterization method that has become one of the most powerful tools for CNT analysis due to the rich CNTs properties it can reveal [29]. It probes the molecular vibrations of a material by using the Raman effect, which is a scattering phenomenon of a high energy photon (much larger than the vibrational transition energies) interacting with a vibrational mode. The measurement technique is based on the illumination of the sample with a monochromatic laser beam (with energies ranging from 1.17 eV to 2.71 eV). This monochromatic radiation interacts with the sample molecules and originates a scattered light. In other words, the incident photons lose energy when interacting with a vibrating molecule. Raman spectra present shifts in wavenumber, with respect to the incident light, which can provide information about vibrational or rotational energies of the sample molecules [30].

In carbon-based materials, Raman spectra is used to identify their phonon and electronic structure, as well as the sample imperfections. The different carbon-based structures that exist (graphite, graphene, fullerenes and CNTs) possess very specific features present in their Raman spectra. For the CNTs case, these can be either single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs) [17]. While the first can be considered a monolayer of graphite, i.e. graphene, rolled up into a cylinder in a seamless way, the second are an ensemble of several concentric tubes of different diameters. Both are different structures in the fact they present different properties (electronic, optical, thermal, etc.) [29]. For example, while all MWCNTs are metallic, SWCNTs can be metallic or semiconducting, depending on the chirality of the tube, which is determined by the way the graphene sheet is rolled up [13], [17].

Raman spectroscopy has been used in this thesis as a standard technique to assess whether the grown samples are SWCNTs or MWCNTs [31] and to qualify their structure (e.g. defects content). For these measurements, a 532 nm (2.33 eV) laser was used in a BeTek Raman spectrometer. Fig. 3.14 shows the Raman spectra of two types of CVD grown CNT forests, one containing MWCNTs and the other SWCNTs.

Fig. 3.14. Raman spectra of two different samples containing SWCNTs and MWCNTs.

A detailed description of the specific Raman features that differentiate SWCNTs from MWCNTs can be found in [29]. As a summary, these are:

- 1) Presence of the radial breathing mode (RBM) at $100 - 500 \text{ cm}^{-1}$. An out-of-plane phonon mode for which all carbon atoms move in the radial direction. It is inversely proportional to the tube diameter of the SWCNTs. This band is the most important SWCNTs fingerprint.
- 2) Presence of a low intensity D peak at 1350 cm^{-1} (compared to the G band). This peak is associated to the defects present in the sample. In MWCNTs the D band intensity is comparable to the G band one.
- 3) Presence of very intense G peak. This peak is derived from the graphite-like in-plane mode. It is an intrinsic feature of CNTs closely related to vibrations in all sp^2 carbon materials. For SWCNTs the G band is split in some features around 1580 cm^{-1} , usually G^- at 1570 cm^{-1} and G^+ at 1590 cm^{-1} . In MWCNTs the G band has a single lorentzian peak.
- 4) Presence of the M and iTOLA bands. The first is an overtone of the out-of-plane transverse optic mode and the second a combination of the in-plane transverse optic mode and the longitudinal acoustic mode. These features do not exist in MWCNTs.
- 5) The G' band is a weaker intensity second order harmonic of the D band, present in both SWCNTs and MWCNT, but at different wavenumber.

3.3. Device applications: measurements set-up

To test the developed devices under particular applications, specific measurements set-ups were needed. This section describes the measurements set-ups implemented for testing the behavior of S_0 -LWRs in contact with liquids (and the shear SMRs ones for comparison purposes), the high temperature characterization of SMRs, and the gas sensing applications of SMRs with integrated CNT forests.

3.3.1. In-liquid testing of S_0 -LWRs (comparison with shear-SMRs)

In order to verify the theoretical predictions and test the behavior of 900 MHz S_0 -LWRs in contact with liquids, two sets of aqueous solutions were used with varying mechanical (density ρ and viscosity η) and electrical properties (dielectric permittivity ϵ). The first type were ethylene glycol-water mixtures with ethylene glycol weight in water varying from 0% to 72%. In this case ρ values are in the range of $995 \text{ kg/m}^3 (\text{H}_2\text{O}) - 1087 \text{ kg/m}^3$ and η values in the range of $0.972 \text{ mPa} (\text{H}_2\text{O}) - 4.76 \text{ mPa}$ [32]. The second type were sucrose-water mixtures with sucrose weight in water ranging from 0% to 40%. The ρ and η ranges in this case are $995 \text{ kg/m}^3 (\text{H}_2\text{O}) - 1156 \text{ kg/m}^3$ and

3.3 Device applications: measurements set-ups

0.972 mPa (H₂O) – 4.62 mPa, respectively [32]. These ranges were chosen so they have similar $\rho \cdot \eta$ product for both types of mixtures, but different ρ and η for each value of their product. Ethylene glycol-water mixtures have greater viscosities and lower densities than sucrose-water mixtures. Regarding the relative dielectric permittivity (ϵ_r) of the aqueous solutions, ethylene glycol-water mixtures move in the range $80 > \epsilon_r > 55$ [33] and sucrose-water mixtures within $80 > \epsilon_r > 66$ [34], with ϵ_r decreasing with the amount of solvent in the mixture.

The influence of the liquids varying properties on the device was assessed by monitoring the peak of the real part of the admittance ($\text{Re}(Y)$) through NA measurements. The procedure to analyze each set of solutions consisted in a first test of the device in air and the posterior dispensing of a liquid droplet on the membrane backside cavity, leaving the electrical contacts dry (Fig. 3.15); although this is not a restriction since liquids can be put on top while IDT is on the backside. In order to assess sequentially all solutions, the test started with the less dense and less viscous mixture and then continued with the denser and more viscous ones. This was done to avoid any influence of previous mixtures on the measurement, although after each solution test devices were rinsed in DI water, dried under N₂ flow and their full recovery was tested in air before the next solution assessment. Additionally, before the in-liquid measurements, a short oxygen plasma treatment was applied to the backside part of the devices to reduce hydrophobicity and avoid wetting problems.

Fig. 3.15. In-liquid testing of 900 MHz S_0 -LWRs by droplet dispensing on the backside cavity, leaving the electric contacts dry. Droplet was trapped in the cavity by placing a microscope slide on the backside and slightly pressing the chip on it.

The in-liquid testing of shear SMRs (at similar 900 MHz operating frequencies for comparison purposes) was performed using the same sets of aqueous solutions, although droplet delivery in this case had to be different. While for S_0 -LWRs the top electrical contacts were left dry by contacting the liquid with the device bottom part, for SMRs the liquid droplets had to be dispensed directly on the top electrical contacts (Fig. 3.16). Since the SMRs structure is characterized by a

bottom and top electrode co-planar layout, the conductivity of the liquids can affect the electrical response by including additional parasitic capacitances. However, previous tests with buffer solutions with electrical properties close to the liquid solutions used here, proved that at the GHz operating frequencies, the parasitic influence is negligible [35].

Fig. 3.16. In-liquid testing of 900 MHz shear SMRs. Liquid is dispensed on the top side of the device where electrical contacts are found (bottom electrode is accessed by capacitive coupling).

3.3.2. SMRs characterization at high temperatures

SMRs characterization at high temperatures ($>500^{\circ}\text{C}$) was carried out in two ways. In the first one, the performance of the devices was assessed before and after annealing them for several hours in high vacuum systems. In the second one, in-situ measurements of the devices were performed while annealing them in an open oven (i.e. atmospheric pressure). The first method was systematically used owing to its simplicity. Namely, it required regular NA measurements with calibration for on-wafer probing. However, the second method does not allow on-wafer probing since regular RF cables and GSG probes do not sustain such high temperatures. The RF in-situ characterization at high temperatures requires unavoidably a more complicated set-up. The description below represents the initial attempts for such a set-up.

There are two main problems involved in the in-situ measurement set-up. On one hand, regular RF cables do not sustain very high temperatures. This forced us to develop a home-made rigid RF cable composed of materials able to resist temperatures above 500°C . On the other hand,

3.3 Device applications: measurements set-ups

simply calibration for on-wafer probing cannot be carried out since the device is not accessed directly by regular GSG probes. In an attempt to solve these problems the set-up, shown in Fig. 3.17, was implemented. It was composed of:

- An open oven with thermocouple temperature controller (Fig. 3.17a).
- A home-made rigid 50 ohms coaxial RF cable made of a 1.5 mm in diameter Cu core, a quartz tube forming the dielectric filling, and a stainless steel exterior tube (Fig. 3.17b). The Cu core and the exterior tube were welded to 1 mm in diameter Au probes for the signal and ground contacts, respectively. The contact to the device was achieved by bonding the device to a 50 ohms co-planar micro strip constructed by depositing Au strips on a ceramic substrate. The chip containing the device was placed on a 5 mm-thick ceramic support to avoid capacitive coupling with the metallic RF cable holder (Figs. 3.17c and 3.17d).
- A portable NA (Keysight Fieldfox N9912) connected to the rigid RF cable through a regular low loss flexible one (Fig. 3.17a). The advantage of using this portable NA lies on the possibility it provides for simple calibration when using non-standard adapters (in this case the home-made RF cable) for connecting a DUT, or device under test. Its “QuickCal” option does not require a specific calibration kit, but allows for an open-load calibration where the load in this case were two parallel 100 ohms resistances mounted in a similar way as the devices under test and measured between the Au probes. This calibration allows for S_{11} reflection signals lower than 40 dB, which can be considered acceptable for this set-up. Additionally, the port extensions values variations were used for curve corrections.

Since the devices were tested at atmospheric pressure with air contact, a 500 nm-thick SiO₂ protective layer was deposited on top after the chip was bonded to the micro-strip adapter (Fig. 2.17d).

The portable NA was connected to a PC for spectra acquisition and resonant frequency tracking. For that the maximum of the $\text{Re}(Y)$ was acquired around the resonant frequency with a bandwidth of 20 MHz (around 1.5 KHz frequency spacing using 12500 data points) and fitted to an eighth degree polynomial. The roots of its first derivative were calculated and the resonant frequency identified. This procedure was implemented in a LabView® application which allows a measurement of the resonant frequency with around 2 kHz accuracy.

Fig. 3.17. Measurement set-up for the high temperature in-situ characterization of SMRs: (a) whole set-up composed of the open oven, the home-made rigid RF cable connected to the low loss flexible one, and the portable NA; (b) close view of the rigid RF cable; (c) rigid cable holder where its Au probes are connected to an Au coplanar micro-strip to which the device is bonded, and (d) close view of the bonded devices where the SiO₂ capping layer is observed.

3.3.3. SMRs with integrated CNT forests: gas sensing applications

A proof of concept of the application of SMRs with integrated CNT forest for gas sensing applications has been carried out by detecting volatile organic compounds (VOCs), more particularly ethanol. For the test, the CNT forests were functionalized by O₂ plasma treatments after they were grown on the top electrodes of the devices. The measurement set-up for the VOC detection is shown in Fig. 3.18. The devices were placed in a small chamber where GSG probing

3.3 Device applications: measurements set-ups

access was achieved through an open hole on the top side and VOC supply controlled through an MQ-3 alcohol sensor. To obtain VOC vapors a bubbling technique was used by flowing pure N₂ into a container filled with the liquid VOC. For diluting and chamber purging, a second N₂ channel was integrated. Tracking of the device response under different VOC concentrations was performed using the same technique described in the previous section. To avoid condensation of the vapors on the device surface the samples were placed on a heater made of a temperature controlled Peltier cell. Temperature of the sample was monitored by a 0.5 mm encapsulated thermocouple attached to the Peltier cell with thermal paste. The temperature during measurements was fixed at around 28°C, some degrees over the ambient temperature by using a PID temperature controller. The value of the fixed temperature was chosen as the one assuring no detection of vapors on devices without CNTs.

Fig. 3.18. Measurement set-up for VOC detection in SMRs with integrated CNT forests. (a) Set-up sketch, (b) actual set-up, and (c) close view of the chamber where the samples are placed and vapors introduced (RF probe, alcohol MQ-3 sensor and Peltier cell are clearly observed).

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S_0 mode Lamb wave resonators for in-liquid applications

This chapter presents the detailed description of the in-liquid sensing mechanisms of S_0 -LWRs. Their sensitivity features towards the liquid density, viscosity and dielectric permittivity are first obtained by FEM simulations and experimentally verified with different aqueous solutions. A comparison with shear mode FBARs working in liquid is additionally included having in mind the technological feasibility.

As introduced in Chapter 1, flexural plate wave (FPW) devices have been the most studied type of Lamb wave devices, particularly for in-liquid sensing [1]–[3]. These devices excite the A_0 Lamb mode, which for specific values of the product between the operating frequency and the membrane thickness, exhibits a propagation velocity lower than the speed of compressional waves in liquid (e.g. the speed of sound in water is ~ 1500 m/s) [4]. This condition prevents acoustic radiation of this mode when the device is contacted by liquid, although it has a considerable vertical component (see Fig. 1.5). Despite their spread use, FPW devices are based on delay line configurations at low frequencies (generally lower than 100 MHz), which, as discussed in Chapter 1, have disadvantages in terms of insertion loss or Q factor [5]. Recently, Lamb wave resonators (LWRs) have appeared as a potential alternative [6]–[9]. More particularly, LWRs exploiting the S_0 mode have proven high mass sensitivity in gaseous media [10], [11]; however their potential for in-liquid operation has been scarcely studied. The predominant extensional component of the S_0 mode, which is little affected by the presence of liquid, makes them suitable candidates for operation in this medium [4], [12]–[15].

In this chapter, the specific sensing mechanisms of AlN-based S_0 -LWRs operating at 900 MHz in liquid environments, are theoretically and experimentally assessed. Initially, their interaction with liquids is studied through FEM analysis by developing a model considering both the mechanical and electrical interactions. The response of the devices to variations in the mechanical properties of the liquid (density (ρ) and viscosity (η)) is analyzed in first place. As in typical shear mode devices [2], the values of the density viscosity product have strong influence on the device response due to the predominant extensional component of the S_0 mode. Subsequently, the sensitivity of the devices to electrical variations in the liquid, particularly dielectric permittivity (ϵ) variations, is assessed. The theoretical predictions are verified through experiments, and at the end, a comparison with the widely used shear mode FBARs, is performed.

4.1. In-liquid behavior predicted by FEM modelling

The acoustic interaction between a piezoelectric device and a structure can be simulated in Comsol with the pre-defined “acoustic-structure interaction” branch. However, with this method only the interaction of pressure waves is considered. In the case of piezoelectric devices contacted by liquid and having a predominant shear component, the main acoustic coupling phenomenon is through shear stresses (e.g. viscous coupling). Hence the need for a FEM model properly describing such interaction.

In this thesis a specific 2D FEM model, using only the “piezoelectric devices branch”, has been developed to study the interaction of S_0 -LWRs in contact with liquids. The model is an extension of the un-perturbed S_0 -LWR model presented in Chapter 2. It includes now a liquid domain on the backside of the AlN membrane, and a “perfectly matched layer” (PML) underneath. The latter emulates a realistic semi-infinite domain by completely absorbing the acoustic energy transmitted to the liquid (see Fig. 4.1a). The boundary conditions are the same than those of the un-perturbed model (lateral continuity and voltage applied to the electrodes) except for the new AlN membrane-liquid interface. The electrical potential of this interface is set to 0 V (Fig. 4.1b) or left opened (Fig. 4.1c). The first condition shields the device from electrical variations in the liquid (ϵ and conductivity), therefore is used to study only the influence of ρ and η variations. Experimentally, the independent detection of the liquid mechanical properties is performed by including a bottom metallic layer (in this case a 100 nm-thick Mo film). Thereby, the theoretical study considers two structures: (1) with a Mo bottom layer (floating bottom electrode), and (2) without it (see Fig. 4.1b). The second condition, i.e. electrically opened interface (Fig. 4.1c) allows simultaneous detection of mechanical and electrical properties of the liquid. For the experimental verification, the influence of the electrical properties alone can be

determined by extracting the mechanical sensitivity obtained when no bottom electrode is included.

The thicknesses of the liquid and PML domains were set to the arbitrary values of $11\text{ }\mu\text{m}$ and $3\text{ }\mu\text{m}$, respectively. These values are arbitrary in the sense they are set large in excess to ensure the semi-infinite condition, however they are not restricted. Moreover, if a fine optimization of computer resources is pursued, these thicknesses should be reduced. The lower limits of their values should guarantee the complete absorption of the outgoing waves in the PML and a thickness larger than the penetration depth of the shear component in the liquid domain [2]. Regarding the mesh characteristics, the same criterion introduced in Chapter 2 is applied, i.e. the number of elements, or cells, per λ should be at least 8. For an operating frequency of $\sim 900\text{ MHz}$ and a sound speed in water of $\sim 1500\text{ m/s}$ we have $\lambda = 1.6\text{ }\mu\text{m}$. For example, in the $11\text{ }\mu\text{m}$ -thick liquid domain we have $\sim 7\lambda$, therefore the minimum number of elements in that domain should be 56

Fig. 4.1. (a) Geometry and boundary conditions of the 2D FEM S_0 -LWR – liquid model. It includes the S_0 -LWR primitive cell composed of a $2\text{ }\mu\text{m}$ -thick AlN membrane with an IDT pair, and a liquid domain formed by a $11\text{ }\mu\text{m}$ -thick liquid layer and its corresponding PML ($3\text{ }\mu\text{m}$ -thick). (b) To sense the mechanical properties of the liquid two structures are used: (1) without floating bottom electrode (0 V applied to the bottom AlN interface for electrical shielding), and (2) with a 100 nm -thick Mo floating bottom electrode set at 0 V to simulate real experiments. (c) For electrical properties sensing the bottom AlN interface is left opened.

4.1.1. Liquid model

The liquid domain was modeled as a linear elastic and electric material. This allows varying its mechanical and electrical properties at the same time. S_0 -LWRs have a strong shear component and a smaller vertical one, being the interaction of the first one with the liquid the predominant. Nevertheless, the small vertical component also couples a small part of the energy to the liquid in form of compressional waves. To accurately simulate the coupling of both compressional and shear waves, the liquid was mechanically assumed as nearly incompressible material. This means that its Poisson's ratio is slightly below 0.5. To be noted that, for the perfectly incompressible condition, with a Poisson's ratio of exactly 0.5, the material would undergo only shear deformations preserving its volume under deformation [16], [17].

The mechanical properties of the linear elastic material are defined in the model through the ρ and the bulk (K) and shear (G) moduli values. K and G are defined as follows:

$$\mathbf{K} = K' + jK'' = K(1 + j\mu_B) \quad (4.1)$$

$$\mathbf{G} = G' + jG'' = G(1 + j\eta) \quad (4.2)$$

with their imaginary parts representing losses dependent on the bulk and shear viscosities (μ_B and η , respectively). For perfectly incompressible materials $G'=0$ and $G'' \neq 0$. The nearly incompressible condition is achieved by setting the value of G'' approximately one order of magnitude greater than the value of G' . Considering the frequency dependence $G'' \propto \omega\eta = 2\pi f_0\eta$, the water viscosity value ($\eta = 0.9727$ mPa·s) and the resonant frequency of the device (900 MHz), we have $G'' \sim 5 \cdot 10^6$ Pa, hence we set a value for the real part of $G' = 10^5$ Pa.

The variations of K have a negligible influence on the device response, since, as mentioned, the predominant effect is the viscous coupling. We kept then the value of its real part constant at the water value:

$$K' = c_{H_2O}^2 \cdot \rho_{H_2O} \quad (4.3)$$

where $c_{H_2O} = 1500$ m/s is the speed of sound in water and $\rho_{H_2O} = 995.9$ kg/m³ the water density, both at approximately 25°C [18]. The bulk modulus losses (K'') are defined by the bulk viscosity value, which was also set constant at the water value $\mu_B = 2.47$ mPa·s.

Considering how the elasticity matrix ($C^{(i,j)}$) is defined in Comsol:

$$C^{(i,j)} \rightarrow (1 + j\eta_D^{(i,j)})C^{(i,j)} \quad (4.4)$$

the damping in the linear elastic material is introduced through the anisotropic loss factor (η_D), described by the following symmetric matrix:

$$\eta_D^{(i,j)} = \begin{pmatrix} \eta_D^{(1,1)} & \eta_D^{(1,2)} & \eta_D^{(1,2)} & 0 & 0 & 0 \\ \eta_D^{(1,2)} & \eta_D^{(1,1)} & \eta_D^{(1,2)} & 0 & 0 & 0 \\ \eta_D^{(1,2)} & \eta_D^{(1,2)} & \eta_D^{(1,1)} & 0 & 0 & 0 \\ 0 & 0 & 0 & \eta_D^{(4,4)} & 0 & 0 \\ 0 & 0 & 0 & 0 & \eta_D^{(4,4)} & 0 \\ 0 & 0 & 0 & 0 & 0 & \eta_D^{(4,4)} \end{pmatrix} \quad (4.5)$$

Since $C^{(i,j)}$ can be represented in terms of K and G , the frequency dependence of $\eta_D^{(i,j)}$ can be written using the following equivalences:

$$\eta_D^{(1,1)} = \frac{2\pi f_0(\mu_B + \frac{4}{3}\eta)}{K' + \frac{4}{3}G'} \quad (4.6)$$

$$\eta_D^{(1,2)} = \frac{2\pi f_0(\mu_B - \frac{2}{3}\eta)}{K' - \frac{2}{3}G'} \quad (4.7)$$

$$\eta_D^{(4,4)} = \frac{2\pi f_0\eta}{G'} \quad (4.8)$$

where f_0 is the resonant frequency of the device in water. Since we aim at studying the influence of the density and viscosity variations in the liquid, the variable parameters in the model were ρ and η , while G' , K' and μ_B were kept constant.

Regarding the electrical definition of the liquid, the domain was defined as non-solid and isotropic with its relative permittivity set as user-defined so the influence of its values variations can be studied.

4.1.2. FEM analysis results

4.1.2.1. Mechanical sensing (density and viscosity)

The response of S_0 -LWRs to ρ and η variations in the liquid has been studied by assessing their resonant frequency shifts and their losses. The study has been performed on the two configurations described in Fig. 4.1b, being the first analyzed case the structure including the Mo bottom layer. As an example, Fig 4.2 presents the total displacement field in the structure in the particular case of water. Propagating waves and their complete evanescence can be observed in the liquid environment and the PML, respectively.

Fig. 4.2. Deformation of the S_0 -LWR – water structure represented by the surface total displacement. The contractions-expansions of the membrane allow energy coupling to the liquid environment, which is completely absorbed by the bottom PML.

The independent influence of ρ and η has been assessed by varying ρ while keeping η constant at the water value, and vice versa. Fig. 4.3 presents, under these conditions, the specific sensitivities of the resonant frequency and losses towards $(\rho \cdot \eta)^{0.5}$. The representation of the shifts in frequency vs. $(\rho \cdot \eta)^{0.5}$ is a typical one adopted for the characterization of acoustic wave viscosity sensors. It arises from Kanazawa and Gordon's prediction [19], which states that the frequency shifts of typical QCMs in contact with liquids are proportional to $(\rho \cdot \eta)^{0.5}$. The losses induced in the resonator can be studied through the conductance spectral maximum $[Re(Y)]_{MAX}$ [2]. This

value can be easily monitored and has the same sensitivity as Q . Particularly, losses ($1/Q$) are represented here by $1/[Re(Y)]_{MAX}$.

From the results shown in Fig. 4.3a, we can extract that the frequency sensitivities towards ρ and η have similarities and differences with the shear mode resonators cases: (QCM) [2] or (shear FBARs) [20]. In contrast to shear resonators, the resonant frequency of S_0 -LWRs demonstrates different sensitivities to ρ and η . More specifically, frequency shifts induced by ρ variations alone show a linear dependency on $\rho \cdot \eta$, not on $(\rho \cdot \eta)^{0.5}$, as it occurs in pure shear resonators. Conversely, frequency shifts due to η variations are linearly dependent on $(\rho \cdot \eta)^{0.5}$.

The damping induced on the device and thus the energy loss in the liquid is also specific to ρ and η (see Fig. 4.3b), being more sensitive to changes in ρ . This is in good agreement with Fig. 4.3a, which reveals that increased sensitivities are translated to larger losses (more energy coupled to the liquid means also more energy lost by the resonator).

Fig. 4.3. FEM simulation of the S_0 -LWR sensitivities towards $(\rho \cdot \eta)^{0.5}$. Figure (a) presents the normalized resonant frequency shifts when varying ρ and keeping η constant at the water value (black squares), and vice versa (red circles). Figure (b) presents the normalized losses $(1/[\text{Re}(Y)]_{\text{MAX}})$ sensitivity following the same scheme as in (a). Frequency shifts and losses are normalized to their in-water values.

The specific sensitivities to ρ and to η can be explained by the particular energy coupling to the liquid, shown in Fig. 4.4. The displacement fields of the shear (horizontal and then parallel to the device surface, u_x) and longitudinal (vertical and then perpendicular to the device surface, u_y) components in the liquid environment, are plotted in Fig. 4.4a. The surface total displacements in the entire structure are shown in Fig. 4.4b and Fig. 4.4c for both cases. The S_0 mode has a laterally

standing wave nature with an extensionally predominated elliptical polarization (Fig. 1.5). On one hand, the vertical component of the elliptical polarization couples to the liquid in form of longitudinal plane waves (u_y in Fig. 4.4a and Fig. 4.4b), different than for shear mode resonators in which this component does not exist or is negligible. On the other hand, the major extensional vibration justifies that, as in shear resonators (Fig. 4.5), part of the mechanical energy is stored close to the surface of the membrane due to the strong decaying tail of the shear component in the liquid (Fig. 4.4a) [2]. However, in the S_0 mode, the laterally alternating shear displacements couple part of their energy to the mentioned longitudinal waves propagating into the liquid in a similar manner as the alternating vertical Poisson's expansions and contractions of the membrane [12]. This specific energy coupled to the liquid has a lateral amplitude modulation following the elliptically polarized resonant pattern of Lamb waves. Thus, the observed emitted mode shows also a shear displacement in the liquid that decays along with the major longitudinal component (u_x in Fig. 4.4a and Fig. 4.4c). This indicates superposition of longitudinal waves propagating in oblique directions, which in turn determines the lateral modulation of the wave amplitude. The described specific coupling of the shear component to the liquid bulk is thought to be responsible for the higher sensitivity to ρ than to η in S_0 resonators.

Fig. 4.4. Displacement fields of the shear (u_x) and longitudinal (u_y) components in the liquid environment (a), and their surface total displacements in the entire structure (b and c).

Fig. 4.5. Example of the shear (u_x) and longitudinal (u_y) displacement field components emitted to the liquid by a shear FBAR composed of a tilted AlN membrane (24° tilted with respect to the c -axis) sandwiched between two electrodes (inset). The simulation is performed using the same liquid model as for the S_0 -LWR. Owing to the quasi-shear nature of the mode, very small part of the energy is coupled to propagating longitudinal waves in the liquid (u_y), while most of the energy is stored closed to the surface due to the strong decaying tail of the shear component (u_x).

The S_0 -LWR sensitivity towards the mechanical properties of the liquid has also been studied considering the second structure from Fig. 4.1b, namely without the bottom floating electrode but with the 0 V potential condition applied to the bottom AlN interface. For comparative purposes, frequency sensitivities to mechanical properties using both the topology with and without bottom electrode are presented in Fig. 4.6. The slightly decreased sensitivity when no bottom electrode is included can be explained in terms of acoustic energy redistribution in the resonant cavity [21]. However, in this case, guided mode [22], the lower acoustic velocity of the Mo layer induces acoustic energy redistribution with slightly increased confinement close to the bottom surface.

This in turn provides the device with increased sensitivity to variations occurring at that interface. Additionally, the absolute resonant frequency slightly varies due to the mass loading effect of the Mo layer.

Fig. 4.6. FEM simulation of the S_0 -LWR sensitivities towards $(\rho \cdot \eta)^{0.5}$ for both topologies, with and without the Mo bottom electrode. Black squares represent the normalized resonant frequency shifts with varying ρ and constant η , and red circles represent normalized frequency shifts with varying η and constant ρ . Frequency shifts are normalized to the resonant frequency in water.

4.1.2.2. Electrical sensing (dielectric permittivity)

Besides being sensitive to variations in the mechanical properties of the contacting liquid, S_0 -LWRs can also detect changes in the ϵ of the latter. This electrical influence only happens when no bottom electrode is used, i.e. the electrical shielding is suppressed. The independent sensitivity of S_0 -LWRs to ϵ has been assessed using the electrically-opened topology (Fig. 4.1c) and by varying the relative permittivity ϵ_r ($\epsilon = \epsilon_0 \epsilon_r$) of the liquid. To study the influence of ϵ variations only, ρ and η were kept constant at the water values. The frequency sensitivity towards ϵ is presented in Fig. 4.7.

Fig. 4.7. FEM simulation of the S_0 -LWR frequency sensitivity to the dielectric permittivity of the liquid. Frequency shifts are normalized to the resonant frequency in water.

Similar to the negative frequency shifts produced when increasing the value of the liquid mechanical properties, the frequency shifts when increasing ϵ are negative. To be noted that, for coherence with the subsequent sections, where both mechanical and electrical sensing are considered, in Fig. 4.7 the frequency shifts are normalized to the resonant frequency in water, which has $\epsilon_r = 80$. The frequency shifts in this case can be explained in terms of the major sensing mechanism involved here, which is related to the variation of the k_{eff}^2 of the resonator. In fact, higher values of ϵ in the liquid allow the electric energy (lying on the electric field) to be better stored in the resonator cavity instead of penetrating into the liquid (Fig. 4.8a); the displacement field is related with the electric field through the dielectric permittivity ($\vec{D} = \epsilon \cdot \vec{E}$). In this way, larger part of the electric energy can be coupled to mechanical in the piezoelectric layer, increasing in turn k_{eff}^2 (Fig. 4.8b). This effect also influences the static capacitance, which increases in the presence of liquids with high ϵ . In Fig. 4.8b this effect is evident with the relative increase of admittance at lower frequencies away from resonance. An increase in static capacitance usually decreases k_{eff}^2 , generating an opposite frequency shift as compared to the one determined by the major sensing mechanism present here. In terms of the circuitual BVD model introduced in Chapter 2, the major sensing mechanism induces changes in the motional capacitance, while the secondary effect induces changes in static capacitance. Both mechanisms are causing opposite frequency shifts with the effects of the most influent one prevailing. The losses, in this case, do not vary significantly. When sensing ϵ the Q of the device is hardly affected by changes in ϵ as they only influence the electric field.

Fig. 4.8. S_0 -LWR dielectric permittivity sensing mechanism described by (a) the distribution of the surface electric potential inside the resonator for frequencies outside the resonant frequency, and (b) the admittances at different ϵ values.

4.1.2.3. Influence of the membrane thickness on the sensing performance

The sensitivity and overall performance of S_0 -LWRs can be strongly affected by the device geometry. To establish a complete in-liquid sensing framework describing not only the S_0 -LWR sensing mechanisms, but also providing the means for their design in view of performance optimization, the influence of the AlN membrane thickness on the device behavior is also studied.

As introduced in Chapter 1, the performance of a sensor is more fairly described when using not only its sensitivity (S_N) but also its Q and resolution factor (R_F). In this section, the performance (Q , S_N and R_F) of S_0 -LWRs for different membrane thicknesses (d) is studied considering two representative in-liquid cases: ρ sensing and ϵ sensing. For each case of study the characteristic parameters describing the performance of the device are simulated considering a specific measurand variation ($\Delta\rho$ and $\Delta\epsilon$, respectively) and different d/λ values. It is worth mentioning that only d is varied, therefore similar resonant frequency ($\lambda \sim 12 \mu\text{m}$) are maintained; this value is primarily dependent on the electrode pitch. For the calculation of Q , S_N and R_F , Eqs. 2.5, 1.8 and 1.11 are used, respectively. For convenience, these equations are repeated below:

$$Q_r = \frac{f_r}{(\Delta f)_{FWHM}} \quad (2.5)$$

$$S_N = \frac{\Delta f}{f_0} \frac{1}{\Delta M} \quad (1.8)$$

$$R_F = \frac{3 \cdot 10^{-7}}{Q \cdot S_N} \quad (1.11)$$

First of all, we can assess the membrane thickness influence on Q when the contacting liquid is water, with ρ , η and ε maintained constants at the water values. Fig. 4.9 presents the variations of Q (normalized to the value of Q when d is 2 μm) with varying d . The lowest Q values are observed for the thinnest and thickest membranes. For thin membranes a greater part of the energy is lost in the liquid, compared to the one stored in the membrane; coupling to the liquid is through the surface while stored energy depends also on the membrane thickness. The thickest membranes provide lower Q values because of the increased vertical displacement of the Lamb wave and therefore increased direct coupling to the liquid through the longitudinal component of the elliptical polarization.

Fig. 4.9. Simulated results of the variation of Q with membrane thickness. The adjacent liquid is considered to be water with its ρ and ε maintained constant at the water values. Q values are normalized to their value when $d = 2 \mu\text{m}$.

Considering the Q variations with membrane thickness when the device is contacted by water, we can calculate now the normalized sensitivities and resolution factors for the mentioned cases (density and dielectric permittivity sensing). In the first case, a variation of $\Delta\rho = +2000 \text{ kg/m}^3$ is set at constants η_{H20} and ε_{H20} with ρ_{H20} being the initial value. Fig. 4.10 shows the shifts of S_N and

R_F with d variations. S_N and R_F are normalized to their values at $d = 2 \mu\text{m}$. The lowest R_F when sensing ρ is obtained for the thinnest membrane ($d/\lambda = 0.08$). However, the evolution of Q showed that a very thin membrane does not sustain high values of Q . Nevertheless, sensitivity to ρ is very large in this case, contributing in a larger proportion than Q to lower values of R_F . Membranes thinner than $1 \mu\text{m}$ ($d/\lambda = 0.08$) are not considered because of the possible technological complications related to membrane fragility. For the thicker membranes S_N is lower, which further contributes to the higher values of R_F .

Fig. 4.10. Simulated results of S_N and R_F for different membrane thicknesses and a variation in the liquid density of $\Delta\rho = +2000 \text{ kg/m}^3$. η_{H2O} and ε_{H2O} are kept constant to the water values. All data are normalized to their values when $d = 2 \mu\text{m}$.

The second case, when the dielectric constant of the liquid is varied in $\Delta\varepsilon = 20$, but ρ_{H2O} and η_{H2O} are kept constant, is plotted in Fig 4.11. Here a similar phenomenon occurs, however S_N saturates for $d/\lambda > 0.2$. A thicker membrane implies a lower relative influence of the electric field confinement on the frequency variation. The percentage of the electric field reaching the liquid decreases with increased membrane thickness.

Fig. 4.11. Simulated results of S_N and R_F for different membrane thicknesses and a variation in the liquid dielectric constant of $\Delta\epsilon = +20$. η_{H2O} and ρ_{H2O} are kept constant to the water values. All data are normalized to their values at $d = 2 \mu\text{m}$.

Summarizing, in both cases the lowest (best) resolution is obtained for the thinnest considered membrane $d/\lambda = 0.08$. For proper optimization we have to look around the point where the highest Q is obtained (high Q values are preferable since this parameter is directly related to the dynamic range of measurements in oscillator based electronics). A good trade-off between S_N and Q when sensing ρ and ϵ can be suggested slightly below the maximum Q factor, i.e. for $0.12 < d/\lambda < 0.17$, where the membrane is also known to be mechanically stable [23]. The theoretical results discussed here can be useful not only for boosting the performance of S_0 -LWRs as in-liquid physical sensors, but also for the development of biological sensors with controlled sensitivities to the liquid properties (medium in which the gravimetric detection occurs).

4.2. Theory vs. experiments: FEM model validation

A valid framework for the in-liquid sensing features of S_0 -LWRs can only be established if the proposed theoretical FEM model is verified. This section presents experimental measurements that support the in-liquid behavior predictions.

To assess both mechanical and electrical sensing principles two types of devices were manufactured following the route described in Section 3.1.3.1. The first one without bottom electrode and the second one with a 100 nm-thick sputtered Mo bottom layer. The electrical responses in air and DI water of both devices are plotted in Figs. 4.12a and 4.12b, respectively. By comparing their responses in air (Fig. 4.12a), we observe that the bottom Mo layer induces an expected shift towards lower frequencies due to the mass loading effect and a better excitation efficiency due to electric field confinement in the piezoelectric layer. Q factor is slightly decreased because of possible stress levels induced by the metallic layer [24]. The obtained Q values for these devices are in the range of previously reported results [10]. It has been demonstrated before that Q enhancement can be achieved by tuning the number of strips in the IDT or by improving the reflectivity of the grating, among other methods [25]. Spurious responses appearing from edge reflections (ripples in Fig. 4.12a) can be suppressed by “bus-bar” engineering [26]. The similar values of Q for both topologies when they are put in contact with water (Fig. 4.12b) sets clear that the performance when working in liquid is determined to a large extent by the liquid losses. In this situation, the pronounced shift in resonant frequency appearing in the device without the bottom metallic layer when contacted by water (blue curve comparison between Fig. 4.12a and Fig. 4.12b) is attributed to the increased static capacitance effect, namely the described sensing mechanism towards ε prevails (Figs. 4.7 and 4.8).

Fig. 4.12. Electrical responses of the manufactured S_0 -LWRs with both topologies (with and without 100 nm-thick floating Mo bottom layer) in air (a) and DI water (b).

Two sets of solute-water mixtures, with different ρ , η and ε , were used to verify the influence of their variations on the S_0 -LWRs response. The aqueous solutions are ethylene glycol-water mixtures and sucrose-water mixtures. Their weight concentrations in DI water and the corresponding ρ , η and ε variations are summarized in Table 4.1 [18]. The aqueous solutions were chosen so that both kinds of mixtures have similar $\rho \cdot \eta$ for each concentrations but with higher ρ (sucrose) and higher η (ethylene glycol), in each case. Additionally, ethylene glycol-water mixtures have increased ε variations.

TABLE 4.1 Concentrations of the aqueous solutions used in the experiments

Solute	Ethylene glycol	Sucrose
Concentration [%w in H ₂ O]	0 - 72	0 - 40
Density [kg/m ³]	995 - 1087	995 - 1156
Viscosity [mPa·s]	0.972 - 4.76	0.972 - 4.62
Rel. Permittivity	80 - 55	80 - 66

The measurement technique, for both topologies, consisted in the one described in Section 3.3.1, by which a droplet of each mixture is fed to the backside cavity of the device. To be noted that the concentration of a specific solute in water modifies all three parameters (ρ , η and ϵ), therefore we are not in the exact case of our previous simulations where one parameter is kept constant while the others are modified. For a proper comparison between the experimental results and the theoretical predictions, now we simulate the specific $\rho \cdot \eta$ values of each mixture, considering ϵ variations only when using the open bottom topology. The following sections present the mechanical and electrical sensing results.

4.2.1. Mechanical sensing (density and viscosity)

The simulated and experimental results using the devices with the Mo bottom electrode, where only $\rho \cdot \eta$ variations are sensed, are shown in Fig. 4.13. In this case both ρ and η are varied for each solution. We observe a relatively good agreement between theory and experiments. However, the different sensitivity to ρ than to η predicted by the FEM model is not appreciable. Both curves are very close even if sucrose-water mixtures have relatively higher densities. The fact that shifts in frequency are so close is explained by the maximum values of ρ we are using, i.e. $\rho = 1156 \text{ kg/m}^3$ for 40% sucrose weight in water. Namely, we are varying η values in a wide range (1 to 4 mPa·s) while ρ can be considered constant at values no greater than 1156 kg/m^3 .

Fig. 4.13. Experimental and FEM simulations of the liquid mechanical influence on (a) the S_0 -LWR resonant frequency and (b) its losses. For both experiments and simulation a bottom 100 nm-thick Mo layer (with 0 V potential in the simulation) is used to screen the electrical influence of the liquids. Each point corresponds to a specific mixture (ethylene glycol-water or sucrose-water mixtures) with a specific $\rho\eta$ value. Frequency shifts and losses are normalized to their in-water values.

A simulation considering such big changes in η and the maximum value used for ρ can explain the results. This is shown in Fig. 4.14, where frequency shifts and induced losses are plotted for η variations in the same ranges as before but considering $\rho = 1156 \text{ kg/m}^3$ (blue triangles). We observe that this curve is very close to the initial red curve (for both frequency shifts and losses), where ρ is kept constant to the water value. Thereby, what we see is that very small variations of

ρ are negligible regarding mechanical sensitivity since the large variations of η predominate. This is explained by the way the energy gets coupled to the liquid bulk through stress gradients dependent on η (non-existent in regular pure shear resonators) (Fig 4.4), which actually provides the device with the increased sensitivity to ρ . An increased sensitivity to ρ would be measurable if low values of η were used, but that is rarely the case of real aqueous mixtures, which present large variations in η but an almost constant ρ .

Fig. 4.14. FEM simulation of the S₀-LWR sensitivities towards ρ and η with the additional curve at constant $\rho = 1156$ kg/m³. Figure (a) presents the normalized resonant frequency shifts when varying ρ and keeping η constant at the water value (black squares), and vice versa (red circles). The curve at constant $\rho = 1156$ kg/m³ (blue triangles) represents the big η variations and the maximum ρ value used experimentally. Figure (b) presents the normalized loss ($1/[\text{Re}(Y)]_{\text{MAX}}$) sensitivity following the same scheme as in (a). Frequency shifts and losses are normalized to their in-water values.

4.2.2. Electrical sensing (dielectric permittivity)

For the experimental electrical sensing the electrically-open configuration was used (Fig. 4.1c). As in the previous section, the simulation was done considering the $\rho \cdot \eta$ values of each mixture, however the value of the dielectric permittivity for each mixture was also included. For convenience, Fig. 4.15 reminds the theoretical frequency shifts expected when varying ϵ_r in the liquid (as shown in Fig. 4.7). In this figure the relative permittivities for the maximum concentrations of ethylene glycol-water and sucrose-water mixtures are marked. Ethylene glycol-water solutions have greater ϵ_r than sucrose-water solutions, i.e. the maximum concentration of ethylene glycol (72%) has around $\epsilon_r = 55$ and the maximum concentration of sucrose (40%) around $\epsilon_r = 66$. Then, we expect influences of $\Delta f \sim +580$ ppm and $\Delta f \sim +300$ ppm for ethylene glycol and sucrose-water mixtures, respectively.

Fig. 4.15. Theoretical S_0 -LWR frequency sensitivity to the dielectric permittivity of the liquid while keeping ρ and η constant to the water values. Frequency shifts are normalized to the value of the resonant frequency in water. On the top of the figure the maximum concentrations are linked with their corresponding dielectric permittivity.

The response of S_0 -LWRs to each mixture is presented in Fig. 4.16. FEM simulations and experimental results are in very good agreement showing a clear difference between ethylene glycol and sucrose solutions. With electrically non-isolated devices we have now a superimposed influence of both negative and positive Δf arising from the mechanical and electrical sensing mechanisms, respectively. On one hand, for an ethylene glycol concentration of 72% the predicted

$\Delta f \sim -850$ ppm, obtained only due to $\rho \cdot \eta$ influences (Fig. 4.13a), is deviated $|\Delta f| \sim 650$ ppm towards positive values. On the other hand, at 40% of sucrose in water, the same prediction from Fig. 4.13a is deviated $|\Delta f| \sim 250$ ppm. We have also to consider that we are using devices without the bottom Mo layer, which makes them slightly less sensitive towards ρ and η (see Fig. 4.6). Particularly, from Fig. 4.6 we can extract sensitivities to ρ and η of about $\Delta f \sim 50$ ppm lower. Knowing this, the obtained deviations from the pure mechanical influence are in good agreement with the predictions from Fig. 4.15.

Fig. 4.16. Experimental and FEM simulations results regarding the influence of the mechanical and electrical properties of the liquid solutions on the electrically-opened S_0 -LWR. Frequency shifts are normalized to in-water results.

4.3. S_0 -LWRs vs. shear FBARs for in-liquid applications

The previous sections have demonstrated the potential of S_0 -LWRs for in-liquid operation. As mentioned, this is useful not only for their application as physical sensors, but also as biological sensors, considering their already proven high mass sensitivity [23]. Their behavior as pure physical sensors, particularly their sensitivity towards ρ and η (i.e. $(\rho \cdot \eta)^{0.5}$), can be compared to previously studied EA viscosity sensors. We can consider the sensitivity value (Eq. 1.8) as the normalized frequency shifts in ppm per unit of $(\rho \cdot \eta)^{0.5}$ kg·m⁻²·s^{-0.5}. In this context, with our 900 MHz S_0 -LWR we obtain a sensitivity of ~ 653 ppm/kg·m⁻²·s^{-0.5} (Fig. 4.3a). For example, the $(\rho \cdot \eta)^{0.5}$ sensitivity obtained by Martin *et al.* with a typical QCM operating at 4.975 MHz [27], was of about 163 ppm/kg·m⁻²·s^{-0.5}, while the one obtained by Weber *et al.* using a shear ZnO SMR with Pt electrodes and operated at 800 MHz [28], of ~ 830 ppm/kg·m⁻²·s^{-0.5}. The low sensitivity of

QCMs evidence again the higher potential of thin film devices (TEA) as sensors. The slightly increased sensitivity demonstrated by the ZnO SMR, compared with the S₀-LWR, may be related to the device configuration, which as we will see in the next section, strongly affects the sensing performance of TEA devices.

Since shear mode FBARs are the direct thin film counterparts of S₀-LWRs, being these first the most studied TEA devices towards in-liquid applications [20], [29], [30], this section and the following aim at performing a deeper comparison between the in-liquid performances of the herein studied S₀-LWRs and the shear mode FBARs. Particularly, in this section S₀-LWRs are compared theoretically and experimentally with AlN based SMRs operating at the same resonant frequency (~ 900 MHz). Such condition is assumed for a fair comparison, since it is presumed that the noise floor is determined mostly by the frequency dependent attenuation in liquid ($\omega\eta$) [31]. Comparing sensors at the same operating frequency eliminates *ab initio* frequency dependent effects. Theoretically, the comparative study is performed by applying the developed FEM model on the SMRs. The model was applied before to suspended shear mode FBARs (Fig.4.5), thus its suitability for shear mode SMRs is also expected; suspended FBARs and SMRs have the same sensing principles.

The structure of the 900 MHz shear mode SMR consists of an acoustic reflector made of five 741 nm-thick porous SiO₂/ 872 nm-thick Mo alternating layers on a Si wafer, a 160 nm-thick Ir bottom electrode, a 1.6 μm -thick tilted AlN piezoelectric film (with $\sim 24^\circ$ *c*-axis tilt), and a 500 nm-thick Mo top electrode. The design of this device is not optimized due to technological problems arising from the AlN tilted grain deposition. Tilted grain AlN layers thicker than 1.6 μm are hard to be obtained owing to the in plane residual stress that the film develops during the deposition process. Therefore, to achieve a low resonant frequency of 900 MHz the top electrode has to be very thick. These practical issues are discussed in Section 4.3.1. Fig. 4.17 shows the simulated displacement of the SMR structure when a liquid layer is placed on the top electrode. As in the S₀-LWR case, a PML for the complete absorption of outgoing acoustic waves in the liquid, is included. Additionally, a PML for the Si domain, representing a semi-infinite Si wafer, is also included.

Fig. 4.17. Surface total displacement of the 900 MHz shear mode SMR calculated by FEM. The structure of the SMR is composed of an acoustic reflector placed on a Si domain with an absorbing PML (representing the semi-infinite Si wafer), a tilted AlN layer sandwiched between two electrodes and a liquid domain with a PML on top. For the piezoelectric AlN, a rotated system with a 24° rotation about an out-of-plane axis is set. Continuous boundary conditions are applied on the structure sides. 1 V and ground interfaces conditions are applied on the top and bottom electrodes, respectively.

The manufactured SMRs were obtained following the route from Section 3.1.3.2, where the two-step process for the sputtering of the tilted AlN is the most characteristic step. Fig. 4.18 presents the electrical response of the device in air and with a DI water droplet on top. The performance of the device ($k_{\text{eff}}^2 = 3\%$ and $Q = 380$) is in close agreement with the state of the art [32], [33].

Fig. 4.18. Conductance in air and in DI water of a manufactured shear mode SMR.

To compare the response of SMRs towards ρ and η the same aqueous solutions (ethylene glycol-water and sucrose-water mixtures) were used (Table 4.1). Experimentally, the solutions were tested on the SMRs following the technique described in Section 3.3.1, where a droplet of each mixture is placed directly on the top electrode. The theoretical and experimental responses (frequency shifts and induced losses) of both SMRs and S₀-LWRs are plotted in Fig. 4.19. From these results we can extract that the fabricated shear mode SMRs and S₀-LWRs move in the same range of sensitivity towards the ρ and η of the liquid. However, S₀-LWRs are slightly more sensitive. The lower sensitivity of SMRs could be related to a lower energy concentration at their top surface in contact with the liquid, either because of the possible small portion of acoustic energy penetrating the acoustic reflector [34], [35], or most likely because of the presence of the 500 nm-thick Mo electrode [21]. Related discussions are included in Section 4.3.1.

Fig. 4.19. Experimental and FEM comparison of the p - η sensitivities of 900 MHz shear mode SMRs and S_0 -LWRs. Each point corresponds to a specific mixture (ethylene glycol-water or sucrose-water solutions) with a specific p - η value. Frequency shifts and losses are normalized to their in-water values.

4.3.1. Comparison considerations: FBARs, SMRs and S_0 -LWRs

In the previous section we compared S_0 -LWRs and shear SMRs at the same resonant frequency (900 MHz) since, for a fair comparison, the frequency dependent effects need to be eliminated [31]. This required the use of a non-optimal SMR structure due to technological limitations. To obtain high quality tilted films (with high c -axis tilt angle) a high stress is unavoidably induced in the AlN films due to the high energy of the process, which for thicker films increases the

4.3 S₀-LWRs vs. shear FBARs for in-liquid applications

delamination risk. Experimentally, this high film stress precluded the use of films with thicknesses higher than $\sim 1.6 \mu\text{m}$, imposing the use of thicker electrodes to obtain the 900 MHz frequency. It seems natural then a discussion regarding the optimal and feasible FBARs structures and the comparison of their in-liquid sensitivities with the S₀-LWRs one.

To complete the comparison from the previous section three types of designs for both suspended FBARs and SMRs have been considered, namely types A, B, and C, whose configurations are detailed in Table 4.2. Configurations A and B represent devices working at 900 MHz. Devices type A are the theoretical straightforward way to obtain 900 MHz and devices type B the ones fabricated in this thesis due to the technological limitations described before. Although a fair comparison at the same resonant frequency is defended in this thesis, it may be claimed that the sensitivity of the electroacoustic devices should be considered at their optimal resonant frequency. Hence, since normally FBARs are meant to work at several GHz, configuration type C considers structures resonating at 2 GHz.

TABLE 4.2 Configurations of the suspended FBARs and SMRs

Type A	tilted AlN [μm]	Bottom electrode	Bottom thickness [nm]	Top electrode	Top thickness [nm]	Frequency [MHz]
FBAR	3	Mo	100	Mo	100	900
SMR	3	Mo	100	Mo	100	900
Type B						
FBAR	1.6	Mo	500	Ir	160	900
SMR	1.6	Ir	160	Mo	500	900
Type C						
FBAR	1	Mo	100	Mo	100	2000
SMR	1	Mo	100	Mo	100	2000

Firstly, we can compare devices at the same resonant frequency, namely FBARs with designs type A and B and the regular S₀-LWR (AlN membrane 2 μm-thick) used in the thesis. The simulated frequency shifts towards $(\rho\eta)^{0.5}$ for all devices are depicted in Fig. 4.20. From these results we observe that, despite small differences, all technologies move in the same range of mechanical sensitivities. A more precise assessment shows that suspended FBARs are always slightly more sensitive than SMRs. As mentioned before, this can be explained in terms of the small part of energy that penetrates the acoustic reflector (Fig. 4.17). This implies that the ratio

between the surface kinetic energy and the total energy in the resonator, which determines the surface sensitivity, becomes effectively smaller. Although the energy penetrating the acoustic reflector is considerably small $< 0.02\%$, it seems to affect in a certain amount the sensitivity of the device. In suspended FBARs, at the same frequency, energy is effectively localized in a smaller cavity thus promoting larger ratio between the surface kinetic energy and the total energy in the resonator. The difference arising between designs A and B lies on the fact that thicker electrodes presume larger influence of the electrodes on the sensitivity features. The decrease of sensitivity for both type B FBARs can be explained by the influence of the high acoustic impedance thick electrodes on the acoustic field distribution in the resonant cavity [21]. Although thinner electrodes and thicker tilted AlN imply higher sensitivity, the technological feasibility suggests considering a trade-off between performance and manufacturability. As for the regular S_0 -LWR, when compared to FBARs of type A, their mechanical in-liquid sensitivity lies in the same range as SMRs while being less sensitive than FBARs, even though they are also suspended membrane type. When comparing now the feasible design B, we observe that S_0 -LWRs are slightly more sensitive than both FBARs. Even though suspended FBARs have slightly thinner membranes, which *ab initio* could be assumed to have higher sensitivity, the use of thicker electrodes in contact with the liquid has a bigger negative influence.

Fig. 4.20. FEM simulations of the frequency sensitivities of suspended FBARs, SMRs and S_0 -LWRs to $(\rho\eta)^{0.5}$. Both designs, type A and B, are considered for the FBAR technology, which are compared to the typical 900 MHz S_0 -LWR used in this thesis. Frequency shifts are normalized to the value of the corresponding resonant frequency in DI water.

Secondly, we can compare all devices considering their optimal designs. Suspended FBARs and SMRs of type C resonating at 2 GHz (acoustic reflector in SMRs tuned for shear mode reflection at 2 GHz) represent a technological more feasible design of the FBAR technology. This design suggests higher sensitivities due to the thinner electrodes compared to design B. In this context, if devices with increased sensitivity are to be compared, for S₀-LWRs we saw in Section 4.1.2.3 that thinner AlN membranes (with a certain limitation) promote increased sensitivity. Thereby, S₀-LWRs with a membrane thickness of 1 μm are used for this comparison. To be noted that with this configuration the resonant frequency is still ~900 MHz, since its value is primarily defined by the IDT pitch. Thus we are comparing 2 GHz FBARs with 900 MHz S₀-LWRs. The simulated frequency shifts towards $(\rho\eta)^{0.5}$ for all these devices are depicted in Fig. 4.21.

Fig. 4.21. FEM simulations of the frequency sensitivities of suspended FBARs, SMRs and S₀-LWRs to $(\rho\eta)^{0.5}$ for their optimal configurations. Design type C operating at 2 GHz for the FBAR technology, and S₀-LWRs operating at 900 MHz but with an AlN membrane 1 μm-thick. Frequency shifts are normalized to the value of the corresponding resonant frequency in DI water.

Although FBARs working at twice the frequency of S₀-LWRs were expected to be more sensitive, we observe that in its optimized version (AlN membrane 1 μm-thick) S₀-LWRs are more sensitive even if their resonant frequency is lower. It should be kept in mind that a higher frequency also implies higher losses in the liquid model (Section 4.1.1). This result confirms the initial argument defending a comparative study at similar resonant frequencies.

From these two comparative studies (Figs. 4.20 and 4.21) it can be extracted that, from the technological feasibility imposed by the sputtering systems existing nowadays, S₀-LWRs are

more sensitive to the liquid mechanical properties, in all cases, even when FBARs are operated at twice the resonant frequency. This high frequency has proven to not overcome the sensitivity of S₀-LWRs, but also implies more complicated read-out electronics for the sensors. The high stress induced in thick tilted AlN films should be the only technological restriction considered. Very thin membranes for both S₀-LWRs and suspended FBARs, also imply more fragile devices. All in all, a trade-off between sensing performance and technological feasibility should prevail.

4.4. Summary

This chapter can be summarized as follows:

- A 2D FEM model describing the S₀-LWRs in-liquid sensitivity features has been developed. The model properly accounts for the viscous coupling to the liquid. This model is suitable not only for S₀-LWRs but also for shear mode FBARs.
- FEM simulations have shown that, in contrast to shear mode devices, S₀-LWRs are slightly more sensitive to the liquid density than to its viscosity. This can be explained in terms of the specific coupling to the liquid of the guided S₀ mode, which has a major extensional component but also a vertical one due to the elliptical polarization. The vertical component couples to the liquid in form of longitudinal plane waves, while through the major extensional component part of the mechanical energy is stored close to the surface of the membrane due to the strong decaying tail. Additionally, the laterally alternating shear displacements of the membrane couple part of their energy to the mentioned longitudinal waves, propagating in oblique directions in the liquid. FEM simulations have also proven that S₀-LWRs are sensitive to the dielectric permittivity of the liquid.
- The sensitivity of S₀-LWRs can be optimized by reducing the membrane thickness. However, this also reduces their Q factors, decreasing thus their resolution. Thereby, for optimal performance a proper membrane thickness to wavelength ratio lying in the range $0.12 < d/\lambda < 0.17$, should be considered.
- All FEM predictions have been experimentally verified with manufactured devices.
- The theoretical and experimental comparative study between the shear mode FBAR technology and the studied S₀-LWRs shows that, when operated at the same resonant frequency (900 MHz), both technologies move in the same range of mechanical sensitivities. However, the considered S₀-LWRs are slightly more sensitive when the tilted AlN technological feasibility in FBARs is considered. Thick tilted AlN films are hard to be achieved, thereby thinner AlN films and thicker electrodes are needed to obtain 900 MHz FBARs, which reduces their sensitivity.

- Although the similar operating frequency condition is recommended for comparing the sensing performances of the devices, the optimal designs of both FBARs and S_0 -LWR have been also compared. That is, FBARs working at 2 GHz and S_0 -LWRs working at 900 MHz, in this last case with thinner membranes for improved sensitivity. Even in this case S_0 -LWRs remain superior in sensitivity.

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CNT-based solidly mounted resonators: high temperature applications and gas sensing

The present chapter is devoted to the full integration of vertically-aligned CNTs on the top electrode of SMRs to boost their gravimetric gas sensing performance. The main technological problems involved in the integration are first addressed. Namely, the mechanical stability of SMRs at the high temperatures needed for CNT formation and the CNT growth on specific substrates, particularly heavy metals. Subsequently, the influence of the integration of CNT forest on the device performance is investigated, and finally the viability of CNT-based SMRs gravimetric sensors is demonstrated by detecting ethanol vapors.

One of the aims of this thesis is the integration of CNT forests on SMRs and demonstrate their gas sensing performance. The main drawback of typically-used active layers like SiO₂, Au or different polymers is the limited area for sensing they provide. Tangled CNTs or composites containing CNTs have already been proposed as sensing layers [1]–[4], however the full potential of vertically aligned (forests) CNTs is still unexplored. The high surface area CNT forests offer, together with their wide chemical compatibility, thus ease to be functionalized [5], [6], suggest their use in gravimetric sensors. Despite their potential as active sensing layers, CNT forest could be additionally used as nm-size filter elements [7], as it will be proposed in Chapter 6. Isolation of bioparticles with diameters below 100 nm, like exosomes, has recently become important for disease diagnosis and efficient clinical prognosis. In contrast to ultra-centrifugation techniques or micro-filtering employing lithography-patterned solid elements [8], CNT forest offer controllable

inter-tube distance by tailoring the catalytic nanoparticles, avoiding thus ultra-high resolution lithographic techniques. Hence CNT forests could be employed as both filter element and active sensing layer. This thesis, as a first step towards this dual-application goal, aims at demonstrating the CNT forest sensing potential by integrating them on SMRs. To achieve this, several issues related to the full integration of the CNT forests need to be addressed in first place. On one hand, the integrity of the SMRs has to be guaranteed at the CNT growth temperatures ($> 600^{\circ}\text{C}$). On the other hand, the selective growth of CNTs on the active area of SMRs, particularly on their metallic top electrode, needs to be fully controlled. This chapter describes the approaches followed in the thesis to tackle the two mentioned problems. Finally, a proof of concept of the gravimetric detection of volatile organic compounds with CNT-based SMRs is presented.

5.1. SMRs for high temperature processing

This section addresses the first issue related to the CNT integration on SMRs, that is, the preservation of the device structure and performance at high temperatures. Besides this specific application, SMRs sustaining high temperatures can also be used as sensors capable of operating under the extreme conditions found in some industrial, automotive or aircraft applications. As mentioned in Chapter 1, they can be a simpler alternative to the widely studied LGS-based SAW devices for such applications [9], [10]. Compared with this type of devices, SMRs could offer a solution for the destructive agglomeration suffered by the metallic IDTs in SAW-based structures. The material of choice for these IDTs has been the subject of extensive studies [11]–[14]. In SAW devices, the resonant frequency is related to the IDT geometry, namely the strips pitch [15], [16]; generally, the solution to the electrode degradation at high temperatures is limited to the selection of the most appropriate material, (e.g. Pt, Ru or Ir in different alloys), since modifying the geometry is not a choice. However, in FBARs, and particularly in SMRs, the metal of choice for the top electrode is not restricted to specific metals or alloys; top electrodes of pure Mo, W or Ir, can be used because their possible degradation at high temperatures can be compensated by increasing their thickness at expenses of a reduction of that of the active piezoelectric layer to adjust the resonant frequency [17]. Thicker electrodes offer, in turn, the advantage of reducing the contact resistances. The following sections detail the specific SMR design for proper high temperatures operation and the characterization of the devices in such environments.

5.1.1. Device design

SMRs are multilayered structures composed of a piezoelectric active layer sandwiched between two metallic electrodes and lying over an acoustic reflector. Considering this, the design of SMRs for high temperatures processing must aim at achieving 1) a solid acoustic reflector with

high interlayer adhesion and low mechanical stress, and 2) a low stressed AlN film capable of fitting the curvature variations of the underlying stack induced by thermal dilations.

5.1.1.1. Acoustic reflector

In terms of the acoustic performance, the reflector stack must provide a reflection as high as possible for the specific acoustic mode the device exploits. In this context, the higher the acoustic mismatch between the layers of the stack the higher the reflectivity (see Section 2.2.2). The most typical combinations of low impedance and high impedance materials used in acoustic reflectors are SiO₂/W [17]–[19] or SiO₂/Mo [20]. In these cases, five alternating high and low impedance layers are sufficient for high SMR performance (i.e. to keep most of the energy confined inside the resonant cavity). Other alternatives are fully metallic reflectors [21] or fully insulating reflectors, where instead of W or Mo, AlN or Ta₂O₅ can be used as high impedance materials [17], [22]–[24]. The latter case needs at least seven alternating layers to reach performances similar to the ones of fully-metallic reflectors, although their use is interesting when parasitic effects arising from capacitive coupling to the last metallic layer of the reflector needs to be suppressed [25]. From a structural point of view, more particularly when the reflector has to sustain high temperature variations, the mechanical adhesion and thermal expansion issues need to be addressed too. Therefore, in this regard few things have to be considered: the layers composing the reflector should have a similar coefficient of thermal expansion (CTE) and relatively low stress, the adhesion has to be ensured and fewer layers are preferred. Acoustic reflectors made of five alternating SiO₂/Mo layers appear as good candidates fulfilling both the acoustic performance and mechanical requirements. The CTE of Mo ($4.8 \cdot 10^{-6}$ m/mKA) is closer to the SiO₂ one ($5 \cdot 10^{-6}$ m/mKA), and compared to W, Mo is inherently less stressed.

Different steps were followed to adapt the SiO₂/Mo acoustic reflectors for high temperatures. On one hand, inter-layer adhesion was enhanced by:

1. Setting thermally grown SiO₂ as the lowermost layer of the stack, instead of sputtered SiO₂. This prevents delamination from the initial Si substrate.
2. Including a very thin (15 nm-thick) Ti layer between each acoustic reflector layer.

On the other hand, the optimal Mo and SiO₂ sputtering conditions were assessed pursuing the low stress condition:

- **Mo optimal sputtering deposition**

The standard sputtering deposition conditions presented in Chapter 3 (Table 3.1) for Mo films were varied in order to reduce their residual stress. Different Mo films were sputtered at different pressures on Si/thermal SiO₂/Ti substrates to determine the suitable stress conditions for the first pair of layers in the acoustic reflector stack. The thicknesses of the layers are 620 nm and 629 nm for the thermal SiO₂ and Mo, respectively, representing their actual values in a 2.5 GHz acoustic reflector. Table 4.1 presents the resulting stress for different pressures. To test the adhesion of the Mo films to the thermal SiO₂ substrates, the scotch tape method was applied. This test is typically used as a simple and standard method for this purpose [26]. Table 5.1 indicates whether each film passed the test. Additionally, a thermal test consisting in annealing the samples at 650°C (200°C/min ramp) for 10 minutes was also performed. If the samples sustained this thermal shock is also indicated in the table.

From the obtained results, we observe that increasing the pressure of our sputtering system switches the stress of Mo films from compressive to tensile. However, the differences are not very pronounced considering that the values of the measured stresses are relatively low (< 900 MPa). Since the lowest stressed films are obtained with pressures below 3 mTorr, our choice is a pressure of 2 mTorr, enough for obtaining a slightly tensile stress. For pressures higher than 5 mTorr the films are too stressed to stay adhered to the substrate even at room temperature.

TABLE 5.1. Mo films sputtered at different pressures for high temperature applications			
Presurre [mTorr]	Stress [MPa]¹	Scotch tape	Annealing
1	-146	Yes	Yes
2	+290	Yes	Yes
3	+492	Yes	Yes
5	+885	Yes	No ²

¹ Negative values represent compressive stress while positive represent tensile stress. The stress values presented in this chapter are calculated following Stoney's equation (Eq. 3.1) by considering the specific underlying curvature radio.

² Mo films deposited at pressures higher than 5 mTorr peeled off few hours after deposition, before applying any annealing treatment.

- **SiO₂ optimal sputtering deposition**

Once the suitable conditions for the deposition of Mo selected, the next SiO₂ layer was adapted to the underlying Si/thermal SiO₂/Ti/Mo (2 mTorr)/Ti stack. Although porous-SiO₂ is the typical low impedance material used in our acoustic reflectors [20], it appears not to be the most suitable one for high temperature applications because it becomes denser with temperature and generates

high surface roughness. Additionally, porous-SiO₂ films show a negative temperature coefficient of the elastic constant, while the dense ones show a positive one, partially compensating the negative temperature coefficient of the device resonant frequency [27]. Advantageously, dense-SiO₂ provides smoother surface enhancing thus the adhesion between layers. For these reasons, it is the low impedance material of choice. It is worth noting that the first acoustic layer was already set as dense-SiO₂ by growing it thermally.

Two pressure conditions were tested for the sputtering of dense-SiO₂, the standard of our sputtering system (Table 3.1) and a lower pressure one. Table 5.2 shows the obtained stress values for both pressures. As can be seen, lowering the pressure in this case reduces slightly the film stress. Although both pressures provide low and tensile stress films on this particular substrate, and both passed successfully the scotch and annealing tests, the chosen one is the lowest stressed one, namely, a pressure of 1.15 mTorr. It is worth noting the importance of adapting the stress of the desired material for particular substrates since the first stages of film deposition strongly depend on the substrate nature and determine the final stress. If, for example, we test the stress of these films deposited directly on Si, they will present slight compressive stress, in contrast to the obtained values with the Si/thermal SiO₂/Ti/Mo (2 mTorr) stack.

By using dense-SiO₂, instead of porous-SiO₂, certain degradation of the acoustic reflector performance is *ab initio* expected due to the relatively higher acoustic impedance of the dense-SiO₂ [20]. Nonetheless, porous-SiO₂ films are also densified after exposure to high temperatures. This slight degradation could be compensated by introducing an additional low-high acoustic impedance pair, however a trade-off between acoustic performance and mechanical strength is considered here.

TABLE 5.2. SiO₂ films sputtered at different pressures for high temperature applications

Pressure [mTorr]	Stress [MPa]	Scotch tape	Annealing
3.5	-309	Yes	Yes
1.15	-178	Yes	Yes

The final design of the acoustic reflector has been exhaustively tested under high temperature conditions before including the electrode/AlN/electrode sandwich. Entire 4 inch wafers were used for the deposition of complete reflectors and different parts of the wafers were tested sequentially after 10 minutes annealings at 650°C (200°C/min ramp) followed by time intervals of several hours. All tests were successful.

5.1.1.2. AlN film

Once the suitable deposition conditions for the acoustic reflector materials established and the integrity of the stack at high temperatures tested, the next crucial step is to adapt the AlN film to the designed acoustic reflector. Several annealing tests of complete SMRs, using AlN films deposited in normal conditions (Section 3.1.1.2), revealed that the standard sputtering conditions for AlN deposition are not suitable since the films peel off. This is because the residual stress of the AlN film is slightly high and compressive in the standard deposition conditions. Therefore, controlling the AlN film stress is mandatory. Although AlN film stress can be controlled in different ways, namely, by tuning the sputtering conditions like the substrate temperature or the pressure, the variation of the substrate bias is probably the most straightforward and studied one [28], [29], which prompted us to investigate its effect in this thesis. Table 5.3 shows stress values of 2 μm -thick AlN films deposited directly on Si wafers using several substrate bias values. This first test was performed initially on Si substrates in order to assess the stress tendency as a function of the applied bias. The results of this study were also useful for the fabrication of the Lamb wave resonators described in Chapter 4, since releasing the AlN membrane from the Si substrates requires AlN films with tensile and very low stress. As we see, reducing the bias voltage lowers the film stress. Slight tensile stress starts to appear when using bias values below $|-52|$ V. This tendency can change when AlN films are deposited onto other type of substrates. As far as we are concerned here, our substrates are the designed acoustic reflectors ended with an evaporated Ir film serving as bottom electrode of the resonators. The optimum value of substrate bias in this case lies around $|-53|$ V to obtain nearly stress free AlN films, or even slightly tensile.

TABLE 5.3. Stress of AlN films deposited on Si using different substrate bias values

Bias [V]	Stress [MPa]
-65	-677
-60	-216
-55	-200
-52	+160
-50	+503

The next sections present the results from annealing tests performed on complete devices.

5.1.2. SMR performance after high temperature annealing

Two annealing methods have been used to test the integrity and overall performance of complete devices. The first one consists in annealing them in an UHV system, and the second in

annealing them in the open oven described in Section 3.3.2, where the vacuum was poorer. Sequential thermal cycles were performed using the first system to a total annealing time of 25 hours. Devices were measured before and after each thermal cycle. More than 100 devices, with either Mo or Ir top electrodes, were measured in this initial test; all of them withstood 700°C treatment in vacuum conditions, preserving their structure integrity. Fig. 5.1 shows optical and SEM images of two devices (with Mo and Ir top electrodes) before and after a complete thermal cycle of 25 h in the UHV system. The optical image from Fig. 5.1a reveals that no degradation of the top electrode occurs, i.e. no bubbles or delamination appeared in the surface of the devices. As mentioned before, this is the typical failing factor in SAW-based devices containing thin metallic strips as electrodes [30]. Fig. 5.1b highlights that the integrity of the SMR stack is still preserved after the 25 h thermal cycle (no interdiffusion, cracks, or delamination is observed).

Fig. 5.1. (a) Optical top view image of two SMRs (with Mo and Ir top electrodes) containing the designed high temperature acoustic reflector, before and after a complete 25 h thermal cycle at 700°C, and (b) SEM image of the cross section of a cleaved SMR before and after the same annealing cycle.

Considering now the performance of the resonators as a function of the duration of the thermal cycles, Fig. 5.2 shows that the Q_a increases at initial stages and subsequently stabilizes, whereas k_{eff}^2 remains almost constant during the first stages of the treatments (with a slight increase after short thermal cycles in the case of Ir electrodes) showing some degradation for the longer thermal cycles. The initial enhancement of Q_a and k_{eff}^2 can be explained in terms of the AlN piezoelectricity improvement after a thermal annealing [31]. It is important to mention that Q_r values are not included in the figures because they strongly depend on the series resistance (R_s)

of the resonator. This electrical parameter was significantly affected by the RF contacting probe (GSG standing for ground-signal-ground), which after several measurements provoked damages in the top electrode (Fig. 5.2a) and a significant reduction of Q_r . This is not a thermal effect.

Fig. 5.2. SMRs performance after annealing represented by the evolution of their Q_a and k_{eff}^2 for both, Mo (a) and Ir (b) top electrodes. Inset from (a) shows the cracks appearing on the active probing area after several measurements.

The devices subjected to thermal cycles through the second annealing method, i.e. using the poorer vacuum oven, showed a different behavior compared to that of the devices annealed in the UHV system. In Fig. 5.3 electrical measurements reveal a continuous degradation of the device performance. As in the UHV system, Q_r is degraded (from 530 to 250, in this case) due to sequential probe measurements, whereas k_{eff}^2 values are maintained. However, Q_a is not initially enhanced but starts degrading from the initial stages of the heat treatments (from 360 to 80, in this case). This can be explained by the higher residual pressure in the system containing greater oxygen concentration, which damages the top electrode and AlN layer by oxidizing them. The

decrease in the resonant and anti-resonant frequencies could be explained by the increased weight of the top electrode through oxidation, and by the softening (reduction in elastic constants and then in acoustic velocity) of the AlN layer when contaminated with oxygen. These results set clear that devices working under poor vacuum conditions, containing significant amounts of oxygen, or even in air, should be protected by a capping film. Suitable materials for such purpose could be SiO_2 or Si_3N_4 , among others. It is important to be aware that the tests performed here, involving sequential RF measurements after each cycle, do not represent a realistic use of the devices under high temperature conditions. For that reason, the severe degradation of Q_r is only limited to this particular assessment. In real cases, the device should be bonded to a substrate holder intended for measurements, being the variations in their performance only dependent on the high temperatures and atmospheric conditions. Nevertheless, device bonding also influences the performance, as will be discussed in Section 5.1.3.

Fig. 5.3. Electrical response (impedance and admittance) of an SMR, with Mo top electrode, before annealing and after 5 h and 29 h in the poorer vacuum oven.

5.1.3. SMRs in-situ performance at high temperatures

Integrity tests through pre and post measurements of devices subjected to annealing cycles are of great help for the assessment of the maximum temperature they can sustain and the performance variations they suffer. Nevertheless, a more realistic analysis consists in monitoring the devices during annealing, namely in-situ monitoring. Since a potential application of these devices is as sensors in harsh environments (particularly at very high temperatures), the

knowledge of the device performance under such operation conditions is of paramount importance.

In this thesis most of the efforts were devoted to achieving SMRs sustaining high temperatures, particularly the one needed for CNT growth (650°C). To do that, pre and post annealing tests were mostly studied. However, an initial approach towards in-situ monitoring at high temperatures was also carried out. In this section a description of this first approach, and its results are described. It should be noted that, as a first approach, the techniques employed here can be subjected to further improvement and optimization. Since these tests were performed at atmospheric pressure in an open oven, the SMRs were passivated after bonding with a thin SiO₂ film (see Fig. 3.17d).

The in-situ monitoring of EA devices requires a well-designed measurement set-up. Since the targeted temperatures are very high, normal RF cables and probes cannot be utilized. The initial measurement set-up approach followed in this thesis was described in Section 3.3.2. The fundamental component of the set-up is a home-made rigid coaxial RF cable composed of a Cu core, a fused silica filling, and an outer stainless steel tube. The dimensions were chosen to provide an electrical impedance close to 50 ohms (Fig. 3.17). This cable contacts the device through a co-planar ~50 ohms micro strip to which the device is ultrasonically bonded. The main problems arise from the impossibility of on-wafer probing, the variations in the properties of the materials composing the set-up during annealing, and the parasites that bonding causes in the electrical response of the device. Fig. 5.4 shows the impedance response of a device before and after bonding (measured by on-wafer GSG probes). The small loop formed by the bonding causes parasitic effects (LC). Nevertheless, these can be de-embedded after calibration.

Fig. 5.4. Impedance of the same SMR before and after bonding.

As a simple solution, although not the best, the calibration of the test fixtures is performed through the “QuickCal” option of the used portable network analyzer. The calibration obtained by this method is considered acceptable (S_{11} magnitude < 40 dB) to perform the device characterization. Fig. 5.5 presents the in-situ response of an SMR at three different temperatures, including room temperature. Degradation of the overall response is attributed to the possible variation in the properties (conductivity, permittivity, etc.) of the materials composing the set-up (e.g. RF cable). The parasitic effects generated by the bonding effect were suppressed through calibration.

Fig. 5.5. Impedance of a bonded device, measured through the RF home-made cable, at room temperature (RT), 280°C and 470°C.

The parasitic effects arising from these variations can be readjusted during monitoring by the port extensions option offered by the analyzer. This option allows compensating these equivalent electrical extensions. Fig. 5.6a shows in-situ measurements up to 550°C by employing such port extensions compensation. Parasitic effects are, to a certain degree, cleaned in these measurements, however, above 450°C the signal starts suffering severe degradation. This is attributed to the contact loss that appears at those temperatures between the Al wire of the ultrasonic bonding and the top electrode of the device (in this particular case Mo). The best wire materials found in the literature for high temperature bonding are Pt or Inconel [30], [32], however we did not have the means for using them in this thesis. In all cases, a good adhesion between these metal wires and the top electrode should be guaranteed.

Fig. 5.6. (a) In-situ electrical impedance of an SMR at several temperatures. Parasitic effects arising from possible properties variations of the materials composing the set-up, are compensated by adapting the port extensions during measurements. (b) Resonant frequency shift with temperature in agreement with the typical thermal coefficient of frequency obtained with these devices ($< -25\text{ppm}/^\circ\text{C}$).

Despite the signal degradation above 450°C , the extracted shifts in resonant frequency (Fig. 5.6b) are in good agreement with the thermal coefficients of frequency normally obtained with these kind of devices ($< -25\text{ ppm}/^\circ\text{C}$) [27].

5.2. Growth of carbon nanotube forests

In Chapter 2 the basis of CNT growth was described, which consists in the thermal decomposition of gaseous hydrocarbons activated by catalytic nanoparticles (NPs). As already

mentioned, there are several factors that determine the final structure of a CNT forest. These are some process factors (temperature, proportion and type of gases) or the materials involved (NPs and substrate materials). This section deals with the study of the growth of CNT forests on two types of substrates: 1) piezoelectric films, particularly AlN, and 2) metallic films.

The initial scope of the CNT growth on AlN was their use as both top electrodes and sensing layers. However, this initial idea evolved to the need of growing CNT forests on the metallic top electrodes of the resonators, due to the increased contact resistance appearing when they were used directly on AlN (~ 30 ohms). Nevertheless, the results obtained regarding the CNT growth on this substrate are presented here since AlN can be a potential alternative to the insulating substrates typically used for CNT growth, like Al_2O_3 or SiO_2 [33]. Some of the techniques applied for CNT growth on AlN were adapted later for their growth on metallic films. In contrast to insulating substrates, growing CNTs on metallic substrates is still a pending matter for the CNT researchers. Related works dealing with the growth of CNTs on Cu, Ta, CoSi_2 or TiN [34]–[39] revealed the growth of MWCNTs, pointing out to the diffusion of the catalytic NPs into the bulk of the metallic substrate as the main problem for CNT growth in these type of substrates.

The size and distribution of the NPs determine the morphology of the tubes (number of walls, diameter) and the forest characteristics (number of tubes per unit area or area density). NP formation involves a series of thermally activated processes that compete against each other. To form the NPs, an initial thin catalytic film (e.g. Fe) is deposited on a specific substrate. Once this substrate is placed inside the CVD chamber, the reducing gas (e.g. NH_3) is introduced and the temperature raised. At this point NP formation starts. The first step is the de-wetting of the catalyst from the substrate, which, according to literature, proceeds more easily on substrates of low surface energy than on those of high surface energy. Insulators like Al_2O_3 , for example, have lower surface energy than most of the metals [39]–[41]. At the same time, besides de-wetting, with metallic substrates, the catalyst also starts to diffuse into the substrate bulk. If diffusion is faster than de-wetting, NPs cannot be formed. Additionally, after de-wetting, the NPs start to move across the surface, coalescing and increasing their size. Due to the low thickness (few nm) of the catalyst layer, NPs displaying simultaneously small size and high area density are hard to achieve. Some techniques to promote the growth of small NPs with high area density have already proven to work. These are the multistep deposition of catalysts with intermediate NP formation and stabilization by oxidation [42], the use of non-catalytic films deposited on the catalyst to partially mask the NPs [43], [44], or the use of thin under-layers, between catalyst and substrate, that act as diffusion barriers and prevent NP coalescence by reducing their mobility [44], [45]. A drawback of these under-layers is the contamination of the NPs and the destruction of their functionality (poisoning). Since efficiency and process velocity of all the above-mentioned

phenomena (de-wetting, diffusion, particle mobility and poisoning) are temperature activated, processing conditions (process temperature, temperature ramp, and time) play an essential role in the creation of NPs. The annealing step during NP formation can be of chief importance for the CNT growth on specific substrates, like the metallic ones. However, it is common practice to execute it at the same temperature used for the CNT growth stage, which narrows the leeway to optimize the whole process. In this thesis, the use of a specific under-layer together with the tuning of the NP formation temperature are the exploited techniques, obtaining both MWCNTs and SWCNTs on both types of substrates (AlN and metals).

5.2.1. CNT growth on piezoelectric AlN

The AlN substrates employed for this study are the typical sputtered high quality *c*-oriented films (1 to 2 μm -thick) used in the resonators. The CNT growth on this substrates was studied using Fe as catalyst alone, or combined with different under-layers. Particularly, these are Ti, Cr and Al. Therefore, AlN films were covered with a thin Fe layer or an under-layer/Fe stack evaporated in sequence (without breaking vacuum in the system) at a base pressure lower than 1.5×10^{-7} Torr. Different thicknesses, and their combination, were studied for all materials (1.5 and 2.5 nm for Fe, 2 and 4 nm for Ti, 2 and 4 nm for Cr, and 4 and 8 nm for Al), however only their optimized values are presented here. These are the ones that yielded the best CNT quality (SWCNTs with low defects content). Particularly these thicknesses are 2 nm for Ti and Cr, 8 nm for Al, and 1.5 nm for Fe. These values are optimized for the specific CVD process conditions used here, however they may need to be modified upon process conditions variations, e.g. the C_2H_2 flow rate. All films were evaporated at constant deposition rates controlled by a quartz microbalance. The deposition rate was previously calibrated by assessing the thickness of test samples using XRR measurements. These measurements were also used to extract the actual density of evaporated Fe films exposed to air, which indicated oxidation.

After the evaporation of the under-layers and Fe films, samples were transferred (air transfer) to the LPCVD system and placed onto the pyrolithic carbon heater. As indicated in Section 3.1.2, NH_3 was used as reducing gas and C_2H_2 as carbon source, which is referred to as the best choice for SWCNT growth [46]. A simple scheme of the growth process, including the different temperatures used for the NP formation stage (T_{NP}), the time of each stage and the gases flow rates, is depicted in Fig. 5.7. The process can be summarized as follows:

- 1) It starts with several N_2 purge-vacuum cycles to ensure cleanliness.
- 2) Subsequently, NH_3 is fed into the chamber at a rate of 50 sccm until a pressure of 130 mTorr is reached.

- 3) The samples are heated at 200°C/min to T_{NP} (450°C, 550°C or 650°C) and kept at this temperature for 5 minutes.
- 4) After the NP formation, the temperature is raised to T_{CNT} (650°C) at a rate of 100°C/min.
- 5) Once T_{CNT} is reached the CNT growth starts by adding C_2H_2 at a rate of 50 sccm to form a 1:1 $NH_3:C_2H_2$ admixture at a pressure of 240 mTorr, maintaining these conditions for 10 minutes.
- 6) The samples are cooled down in vacuum.

Fig. 5.7. Stages of the CNT growth process: 1) NP formation using different temperatures, 2) CNT growth and 3) final cool down.

CNT growth was achieved with all under-layers and for all T_{NP} . Slight CNT quality improvement (higher G to D ratio) was observed for $T_{NP} = 650^\circ\text{C}$ for all catalytic stacks. Therefore, only this case is presented here. Each catalytic stack provides CNT forests of different aspect and quality (see Fig. 5.8). While for Fe, Ti/Fe and Al/Fe vertically aligned CNTs were obtained, with Cr/Fe only short and unaligned CNTs grew. Base-growth model was confirmed in all cases by manually removing the CNTs and growing them again. This simple test verifies if NPs are stably anchored to the substrate or are at the tip of the tubes. From Fig. 5.8 we can also extract that the Al/Fe stack allows the growth of the tallest and most packed forest. In addition, Raman spectra reveal that by using Fe, Ti/Fe and Cr/Fe catalysts, forests containing mainly MWCNTs with high defect content (G to D ratios close to 1) are obtained. However, forests with a high SWCNT content are achieved using Al/Fe catalysts. This is evident by the Raman fingerprint of SWCNT described in Section 3.2.3.3 and characterized by: strong RBM peaks, high G to D ratio (around 9.2), G band split, the presence of M and iTOLA peaks and the shift to lower energies of the single component of the 2G peak [46]–[48]. The position of the RBM peaks in this case indicates that the tube diameters are around 1 nm and below (0.7 nm – 0.9 nm) [42].

Fig 5.8. (a) SEM images of CNTs grown from samples with Fe, Ti/Fe, Cr/Fe and Al/Fe stacks at $T_{NP} = T_{CNT} = 650^{\circ}\text{C}$ CNTs. The heights of the forests are 9 μm, 4.5 μm, 21 μm and 63 μm for the Fe, Cr/Fe, Ti/Fe and Al/Fe stacks, respectively. (b) Their corresponding Raman spectra. The inset shows in detail the RBM peaks of the Al/Fe spectrum.

To have a deeper insight into the phenomena occurring with each stack, we should assess the NP formation stage. Test samples of polished AlN were used to form the corresponding NPs, suppressing thus the inherited roughness of the underlying AlN. This was done only for this particular test. In Fig. 5.9a we see AFM images of NPs formed at $T_{NP} = 650^{\circ}\text{C}$ for all stacks, and in Fig. 5.9b their corresponding line shapes representing the surface roughness, before and after

NP formation. Prior to the results discussion, it is important to mention that the AFM images obtained with this equipment are the convolution of the AFM tip diameter (which is 5 nm) and the NP diameter. Thus, the measured NP dimensions are actually an overestimation of their real values. Nevertheless, the results can be used for comparison purposes between samples. From both figures we can see that after annealing, the NPs formed from Cr/Fe have the largest size in both lateral and vertical dimensions, and the NPs obtained from Al/Fe are relatively taller, more defined and denser than the ones formed from Fe or Ti/Fe. Hence, the Al/Fe catalytic system provides the smallest NPs. In addition to the AFM tip convolution effect, the dimensions of the measured NPs are actually larger than the actual Ns dimensions when CNT nucleation starts. This is due to the oxidation of the NPs when they underwent air transfer. XRR measurements corroborated that the density of air transferred Fe NPs is 34% less than that of pure Fe, indicating great oxygen content. It was verified that, even on this samples with oxidized Fe NPs, CNT were able to grow. In this case, NH_3 reduces the NPs removing the excess of oxygen content yield CNTs quality as good as the one when no process breakdown was provoked.

A combination of several effects can explain the growth of high quality SWCNTs on piezoelectric AlN films using the Al/Fe catalytic stack. AlN is a rough substrate due to its columnar grain structure. This has been proven to be useful for inducing small NP formation since it provides sinks for NPs, inhibiting their coalescence through surface diffusion [49], [50]. Fe has proven to favor CNT growth on AlN since it tends to oxidize slightly [51]; moreover, specific bonds between Fe-N and Fe-Al occur, offering NP immobilization [49]. Additionally, the roughness of an Al under-layer increases the amount of sinks for NPs and favors their formation and stabilization in smaller dimensions. The profile lines of the AFM images in Fig. 5.9b set clear that as-deposited Al/Fe films already provide increased roughness compared to the other cases. After annealing, while Al/Fe conserves the initial roughness stabilizing small NPs, too large and less defined NPs are observed for the other cases.

Fig 5.9. (a) AFM images of the NPs formed from each stack (1.5 nm of Fe, 2 nm/1.5 nm of Ti/Fe, 2 nm/1.5 nm of Cr/Fe and 8 nm/1.5 nm of Al/Fe) after 5 min at $T_{NP} = 650^\circ\text{C}$. (b) Their corresponding line profiles representing their surface morphology as-deposited (dotted lines), and after NP formation (solid lines). Traces are arbitrarily shifted for clarity.

Although surface roughness helps low-size NP formation, a complementary explanation on the effect of each under-layer can be given in terms of their surface energy. The latter has been reported to be associated to de-wetting effects and restructuration of Fe to form NPs [40]. The three different under-layers have different surface energies, which influences the NP formation process. The theoretical surface energy of piezoelectric AlN films with wurtzite structure (5.84 J/m^2) is greater than that of Fe (2.4 J/m^2) or that of the under-layers (3.5 J/m^2 , 2.6 J/m^2 and 1.1 J/m^2 for Cr, Ti and Al, respectively) [52]. Considering this, we may think that de-wetting using

only Fe can hardly be achieved. However, the fact that AlN has been in contact with air before catalyst deposition suggests that oxygen incorporation to the surface is possible [49]. This reduces the surface energy of the AlN substrate, since Al-O compounds have very low surface energy (such as 0.1 J/m^2 for Al_2O_3) [39]. The resulting surface energy has not necessarily to be as low as the one shown by Al_2O_3 , since a short exposure to air does not guarantee the formation of this compound. Rather than Al_2O_3 , Al-N-O compounds are formed. A simple test can be carried out to check the surface energy of AlN exposed to air and compare it with that of Al_2O_3 and Ir (3.0 J/m^2). DI water droplets were put on three samples containing Al_2O_3 , AlN and Ir films. The droplet shapes for all cases are shown in Fig. 5.10. The picture reveals that de-wetting of the droplet from the AlN substrate proceeds harder than from Al_2O_3 , since the contact angle between the droplet and the surface is smaller, but easier than from Ir. The greater the surface energy of the substrate the easier to achieve complete wetting of the liquid [53]. This test does not provide quantitative values for the surface energies, but confirms that the surface energy of wurtzite AlN exposed to air is greater than 0.1 J/m^2 and smaller than 3.0 J/m^2 , hence lower than the theoretical value of 5.84 J/m^2 .

Fig. 5.10. Comparison between Al_2O_3 (0.1 J/m^2) – AlN – Ir (3.0 J/m^2) surface energies using a droplet of DI water. Wurtzite AlN surface energy lies between 0.1 J/m^2 – 3.0 J/m^2 .

A scheme of the four situations we are dealing with, namely AlN/Fe, AlN/Cr/Fe, AlN/Ti/Fe and AlN/Al/Fe stacks, is depicted in Fig. 5.11. Now we can consider the estimated surface energy of AlN exposed to air (textured film on top of the AlN represents possible Al:O or Al:N:O compounds) and the corresponding theoretical values of the under-layers and catalyst. The biggest

NPs and worst CNT forests are obtained with the Cr under-layer, which has a surface energy higher than that of Ti and Al. The reason could be the fact that its de-wetting from the AlN substrate proceeds easily and forms big islands (for all T_{NP}) without providing small sites for the formation of Fe NPs. These islands are bigger than the corrugation offered by the AlN surface. Thus Cr/Fe NPs move easily across the surface and Fe NPs are not stabilized. Ti offers lower surface energy than Cr, hence de-wetting from the AlN substrate proceeds hardly preventing the formation of very big islands. The case of Ti/Fe can be extrapolated to the case of Fe alone, as the results obtained for both are very similar. Finally, Al exhibits the lowest surface energy, which does not allow easy de-wetting from the AlN substrate, but is high enough as to provide small nucleation sites for the formation of very small Fe NPs.

The inclusion of Al below the catalyst stack has already proven to promote SWCNT growth on other substrates [50]. Although CNT growth on AlN is possible by using only Fe due to Fe-N and Fe-Al interactions [49], placing an Al under-layer between Fe and AlN provides increased roughness and less mobility for the Fe NPs. This favors the growth of denser and with higher SWCNT content forests.

Fig. 5.11. Scheme considering the theoretical surface energies for all under-layers-catalyst combinations. The textured film on top of the AlN represents possible Al:O or Al:N:O compounds.

5.2.2. CNT growth on metallic films

Several metals were used as substrates (Mo, Ta, W, Au, Cu Ti, and Ir), however the growth of CNT forests was achieved only on Mo, Ir, W and Ta; only their cases are presented here. These metals are suitable materials as top electrodes in EA resonators, therefore the successful results open the way for CNT integration on the devices.

For the study, the metallic films were sputtered on oxidized silicon wafers (thermal oxide) to an oxide thickness of 200 nm. A 10 nm-thick Ti film was included before the metallic films for improving adhesion to the substrate. As in the case of the AlN substrate, different under-layers were studied (Ti, Cr, and Al), being Al the only one that promoted growth with SWCNT content on all substrates by avoiding diffusion of the Fe NPs into the substrate and controlling their surface mobility. A wide range of Al and Fe thicknesses were assessed with the optimal ones being the same as for the AlN case (8 nm for the Al under-layer and 1.5 nm for the Fe catalyst). Only this optimal case is presented here. As for the temperature needed for NP formation (T_{NP}), this step has proved to be crucial for the successful growth on metallic substrates. As mentioned before, usually this annealing step is performed at the same temperature as the CNT growth stage, often exceeding 600°C. Several experiments proved that at these high temperatures, the growth of CNT does not take place on metals, even with the Al/Fe stack. These results prompted us to explore the NP formation at lower temperatures, with special consideration to all the thermally activated processes that take part in the formation of the NPs (catalyst diffusion into the substrate, de-wetting, particle mobility and poisoning). In this context, T_{NP} values below 600°C were appropriated for the growth of CNT forests using the Al/Fe stack on Mo, Ir, W and Ta. Fig. 5.12a presents an example of CNT forests grown on Mo, Ir, W and Ta using the optimal thickness for the Al/Fe stack, $T_{NP} = 450\text{ °C}$ and $T_{CNT} = 650\text{ °C}$, with 5 and 10 min for the NP and CNT growth stages, respectively. The growth process scheme is the same as the one plotted in Fig. 5.7. Their corresponding Raman spectra are shown in Fig. 5.12b. All of them display the RBM mode, characteristic of SWCNTs. In the Raman spectrum corresponding to CNTs grown on Mo substrates, the 2G mode around 2700 cm^{-1} displays a single term and the G to D ratio is 7.9, indicating the highest content of SWCNTs, whereas the double mode that appears for the other metals points out to a mixed composition of SWCNTs and MWCNTs [48].

Fig. 5.12. (a) SEM images of CNT forests grown on 200 nm-thick sputtered Mo, Ir, W and Ta substrates, and (b) their corresponding Raman spectra.

The observed results are again very likely related to the surface energy of the metallic substrates. From the presented data we can deduce that only metals with high surface energy are appropriate for CNT growth. The surface energies of Mo, W, Ta and Ir substrates, over which good-quality CNT forests have been achieved, are 3.0 J/m², 3.68 J/m², 3.15 J/m², and 3.0 J/m², respectively [52]. Conversely, the surface energies of Cu, Ti and Au substrates yielding poor or inexistent CNT forests are 1.83 J/m², 2.52 J/m² and 1.50 J/m², respectively [52]. The high surface energy of Mo, W, Ta and Ir, impedes the complete de-wetting of Al, allowing it to act as a barrier for the diffusion of Fe atoms to the substrate. Additionally, the low surface energy of the Al under-layer (1.16 J/m²) allows the Fe catalyst to de-wet from the Al surface and form NPs; this surface

energy is, however, sufficient to prevent, at the adequate temperature, the Fe NPs to freely move. This promotes the formation of high-area-density and small-size Fe NPs, which originates the growth of dense CNT forests.

To assess the strong influence of the temperature on the NP formation, the case of Mo was studied in more detail since Mo appeared to be the best metallic substrate to promote the growth of CNT forests with high SWCNTs content of high quality. In addition Mo is the top electrode mostly used in this thesis. Nevertheless, the same reasoning applies to the other metals. In Fig. 5.13 we see the surface morphology and roughness, through AFM measurements, of a sample at different stages, namely, as-deposited Mo, after Al/Fe evaporation and after 5 min of NP formation at different T_{NP} (450°C, 550°C and 650°C). Needless to mention again that the AFM images show a convolution between the AFM tip diameter (5 nm) and the NP diameters. As-deposited Mo films exhibit a fine-grain structure without noticeable surface roughness. After the Al/Fe stack evaporation, the roughness of the surface increases slightly, owing to the presence of the Al and Fe films. Fe NPs are clearly formed after annealing at $T_{NP} = 450^\circ\text{C}$; although the size of the particles in the basal plane is similar to that of the Mo/Al/Fe as-deposited case (Fig. 5.13a), their height is considerably larger, as the Fe atoms aggregated forming NPs (Fig. 5.13b). The size of the NPs increases slightly as T_{NP} is raised to 550°C, which is associated to their larger mobility promoting coalescence. Finally, if T_{NP} is increased to 650°C, a larger structure formed by 200 nm-wide NPs appears. This apparently modulates a rough surface formed by 40 nm-wide NPs. This structure can be related to the aggregation of Fe NPs. It was verified that the appearance of the surface covered with an 8 nm-thick Al layer did not change after thermal treatments of 5 min up to 650°C because de-wetting of Al from Mo did not take place. The presence of Al, even at high temperatures, prevents the diffusion of Fe atoms into Mo and hampers the movement of the Fe NPs across the Mo substrate.

Fig. 5.13. (a) AFM images of a 200 nm-thick as-deposited Mo film, after the deposition of 8 nm of Al and 1.5 nm of Fe, after 5 min annealing in NH_3 at 450°C, and after 5 min annealing in NH_3 at 650°C). (b) Their corresponding line profiles representing their surface morphology, with the addition of the 550°C case. Traces are arbitrarily shifted for clarity.

Regarding the subsequent CNT growth stage, for $T_{\text{NP}} = 650^\circ\text{C}$ CNT forests did not grow, while for both 450°C and 550°C, CNT forests containing SWCNTs were obtained. The lack of growth on NPs formed at 650°C is explained in terms of the catalytic deactivation of the Fe NPs owing to inter-diffusion effects of Al and/or Fe atoms. Both $T_{\text{NP}} = 450^\circ\text{C}$ and $T_{\text{NP}} = 550^\circ\text{C}$ provide forests

with very close SWCNTs qualities (i.e. Raman spectra similar to that presented in Fig. 5.12b-Mo).

Once proved SWCNT growth in both cases, the influence of the C_2H_2 flow rate was assessed in order to control the CNT forest height. The importance of the latter is discussed in Section 5.3.2. C_2H_2 flow rates of 12.5, 25, 50 and 75.5 sccm were tested for both T_{NP} cases. The other parameters of the CNT growth stage were maintained the same in all cases ($T_{CNT} = 650^\circ C$ and $t_{CNT} = 10$ min). While for flow rates of 12.5 sccm CNT forests did not grow using $T_{NP} = 450^\circ C$, not even for twice the growth time, for $T_{NP} = 550^\circ C$ 10 μm -tall SWCNT forests were obtained. As for the other flow rates, Fig 5.14 presents the CNT forests heights obtained with $T_{NP} = 450^\circ C$ and $T_{NP} = 550^\circ C$ for C_2H_2 flow rates ranging from 25 sccm to 75.5 sccm. Clearly, taller CNT forests are obtained with $T_{NP} = 550^\circ C$ in all cases. Raman spectra of all forests (not shown here) also prove that, although similar, the SWCNT quality is slightly better for $T_{NP} = 550^\circ C$. The increased height of the forests obtained with $T_{NP} = 550^\circ C$ can be explained in terms of the time elapsed from the NP formation stage to the CNT growth stage (Fig. 5.7). This time is twice in the case of $T_{NP} = 450^\circ C$, which might promote NP coalescence and hence slightly bigger NPs just before CNT growth. This can also explain the case of the 12.5 sccm C_2H_2 flow rate, which proves not to be enough to promote growth on the bigger NPs obtained with $T_{NP} = 450^\circ C$. These results allow for a better CNT height control, needed, as it will be discussed, for the optimal CNT forest integration on SMRs. In this context, forest height can be better controlled with lower C_2H_2 flow rates.

Fig. 5.14. CNT forests height with varying C_2H_2 flow rates for $T_{NP} = 450^\circ C$ and $T_{NP} = 550^\circ C$. In both cases the parameters for the CNT growth stage are the same, $T_{CNT} = 650^\circ C$ and a growth time (t_{CNT}) of 10 min.

5.3. Integration of CNT forests on SMRs

This section deals with the final integration of CNT forests on AlN based SMRs. It includes an explicative route of fabrication and a detailed assessment of the strong influence that CNT forests have on the device performance. Finally, a discussion regarding the trade-off that needs to be considered for optimal device performance and final sensing ability, is added.

5.3.1. Fabrication route

- Initial longitudinal SMR composed of a 120 nm-thick Ir bottom electrode, a 1 μm -thick *c*-oriented AlN, and a 150 nm-thick Mo top electrode (designed SMR structure for high temperature).

- Definition, by a lift-off process, of the CNT growth on only the active top electrode area. The Al/Fe catalyst film is thermally evaporated after the photoresist definition.

- Removal of the photoresist with the catalyst left only on the active area of the device.

- CNT forest growth following the CVD process described in Section 3.1.2.

- SEM top view (left) and cross section (right) of a complete device.

5.3.2. Influence of CNT forests on the device performance

Although foreseen as promising candidates as sensing layers in gravimetric gas sensors, when integrated on SMRs, CNT forests induce certain degradation on the device performance. Fig 5.15 shows the electrical responses of an as-fabricated SMR (bare), after catalyst definition on its active area, after CNT growth, and finally after removing (mechanically) the CNT forest. Besides the impedance responses (Fig 5.15a), the real parts of admittance (Fig 5.15b) and impedance (Fig. 5.15c) are also included. The effects of the CNT integration process on the device are manifold. In first place, we observe the effect of depositing a catalyst thin layer only on the active area of the device, that is, the apparition of a second resonant peak, very close to the initial one, associated to the area on which the catalyst film has been deposited (blue curve in Fig. 5.15). Since our SMR is composed of a metallic-insulating acoustic reflector, this is unavoidable, unless we use a fully insulating reflector and we define the bottom electrode only under the active area, leaving the GSG probing zone on the top electrode piezoelectrically inactive. Although not done here, the study and structural adaptation of fully insulating acoustic reflectors for high temperatures applications is already undergoing and is proposed as a future line of investigation in Chapter 6.

Fig. 5.15. Electrical responses of the same device before and after CNT forest integration.

In second place, after CNT growth (red curve in Fig. 5.15) we observe an overall degradation of both resonant and anti-resonant Q -factors. Particularly, in Fig. 5.15 Q_r degrades from an initial value of 390 corresponding to the bare SMR, to a value of 324 after CNT integration, and Q_a from 478 to 54. Additionally, also occurs. By measuring the electrical response of the device after CNT removal (green curve in Fig. 5.15) we observe that, while at anti-resonance the device is almost completely recovered, at resonance the degradation is still present. This means that the degradation of Q_a is due only to the presence of the CNT forest, while the degradation of Q_r may be originated by the CVD process itself, which probably provokes oxidation or carbonization over

the entire top electrode surface, increasing thus R_s . We can verify this by assessing the response of a test device, namely, a device which has undergone a CVD process but on which the CNTs were not grown. The electrical response of such a device is shown in Fig. 5.16. We observe here that, as expected, the CVD process introduces a considerable degradation of Q_r , while barely influences the anti-resonant behavior. In addition, we also observe an overall frequency shift of about 30 MHz (also seen in Fig 5.15) explained by the possible thin metallic oxide layer on the top electrode. Therefore, the frequency shift observed after growing CNTs is mainly due to the presence of this oxide, but also affected by the presence of the CNTs (in a smaller amount since CNT forests are very light materials). Degradation of k_{eff}^2 does not occur; on the contrary, slight improvement happens due to the mentioned AlN piezoelectricity enhancement after a short thermal treatment (see Section 5.1.2).

Fig. 5.16. Electrical response of a test device (without CNT growth), before and after going through a complete CVD process.

Since the CNT forests directly affect the anti-resonance performance of the device, this physical phenomenon is studied in more detail. The fact that a CNT forest strongly degrades Q_a means that it introduces a path to acoustic energy leakage. To explain such behavior we can hypothesize several effects that might be occurring. First of all, the acoustic reflection at the top electrode-air interface is now reduced since the acoustic impedance of the CNT forest is higher than that of air. Since Q_a is decreased, certain amount of energy is radiated to the forest and does not return back to the resonator. Two reasons may explain this. On one hand, the reflection at the CNT forest-air interface is probably negligible due to poor acoustic impedance mismatch or because the interface is very irregular making the reflection very disperse. On the other hand, the

CNT forest can be considered as a poroelastic material in which the acoustic waves lose directionality due to the inherent inhomogeneity of the propagating medium and they suffer multiple scattering. This, added to the fact that energy dissipation can also be associated to the friction between tubes, could explain the observed degradation in device performance. Nevertheless, the acoustic propagation in CNT forests and its modelling involves more complicated phenomena whose study is beyond this thesis. For example the coupling that needs to be considered between the solid skeleton and fluid phase, or the existence of various acoustic wave types that can propagate inside such structures, like the compressional ones existent in the solid and the fluid and the appearance of a new slow compressional one representing the relative motion between the fluid and the solid frame [54].

From an ideal sensing point of view, taller CNT forests (as the ones employed in Fig 5.15) are more desirable since they offer higher surface area for the targeted species to bind to. However, from Fig. 5.17, we observe that the device performance worsens as forest height increases. After certain height (around 20-30 μm) the degradation reaches a saturated state (Q_a around 50), i.e. forests taller than that will not induce more degradation than the existing one. This could be probably related to the arguments on energy dissipation inside the forest described above, with the possible existence of a specific tube length at which the acoustic waves are almost completely dissipated before reaching the top interface. The tendency presented in Fig. 5.17 is the one observed in the particular case of the frequency and CNT structures used here. It may vary at different frequencies and with different forests.

Fig. 5.17. Degradation of the SMR anti-resonant quality factor (Q_a) with forest height.

Other chief factors that can modify the absorbing behavior and sensing features of CNT forests are the tube area density and the tube type (MWCNT_s or SWCNTs). Increased number of tubes in the forest can imply stronger energy dissipation associated to their friction, and also reduction of the acoustic reflection at the resonator/CNTs interface. With regards to the sensing features, tuning the tube density ultimately determines the dimension of the targets that can penetrate the forests. The in-deep study of forests with varying densities and type of tubes, and their influence on the device performance is proposed as a continuation of this thesis.

Summarizing, the main considerations when integrating CNT forests on SMRs should be:

- Short CNT forests (e.g. $< 5 \mu\text{m}$) are the most appropriate choice to avoid severe degradation of device performance. Species bond to very tall forests might not be detected by the resonator.
- From a sensing point of view, few microns of CNT forest are not ideal, but still have several orders of magnitude higher surface area than regular planar films used as active sensing layers (e.g Au, SiO₂, etc).
- The tube density and the CNT type can also influence the absorbing character of the forests and hence the device sensing features, for example in terms of target dimensions.

Therefore, to take advantage of the integration of CNT forest on SMRs for sensing applications, we should find a trade-off between device performance and detection effectiveness.

5.4. Gravimetric detection using CNT-based SMRs

This section aims at validating the initial hypothesis, namely, the improvement of the gravimetric gas sensing performance of SMRs, by integrating CNT forest to act as active sensing layers. The range of applications of the designed devices is wide and requires specific studies. For now, the scope here is only to prove the viability of this devices as sensors, particularly as ethanol vapor detectors. The latter is classified among the volatile organic compounds (VOC), which are typical targets in gas sensing applications.

The CNT-based SMRs used here are composed of SWCNT forests, less than $5 \mu\text{m}$ tall, grown onto longitudinal mode resonators isolated from the substrate by an acoustic reflector made of alternating layers of SiO₂ and Mo. The device fabrication is detailed in Section 5.3.1. An optical top view of a final device, including its cross-section sketch, is presented in Fig. 5.18.

Fig. 5.18. Structure of a CNT-based SMR for ethanol vapor detection. Top optical view (a) and corresponding cross section (b).

One unavoidable problem we encounter when detecting vapors is their condensation on the surface of the device. This condensation can lead to the deposition of a thin liquid layer which can no longer be considered a gaseous environment, involving phenomena like the radiation of the longitudinal mode to the liquid layer [55]. To solve this problem, we have set the device at a constant temperature, high enough so the condensation is avoided. The measurement setup including this feature is described in Section 3.3.3. To find the proper temperature a previous test with a bare SMR (without CNTs) was monitored when introducing different concentrations of ethanol vapors in the chamber. The room temperature at the measurement moment was 20-21°C and the needed temperature applied to the device to suppress considerably the condensation effect was around 25°C. This temperature was the one subsequently applied to the CNT-based SMRs, and maintained during their ethanol detection test. Fig. 5.19 presents both the frequency shifts produced in a device without CNTs, and in a CNT-based one, where an O₂ plasma was applied to the forest, as explained in Section 3.3.3. The testing process consisted in increasing sequentially the ethanol vapor concentration and cleaning the chamber with pure N₂ after each concentration.

Fig. 5.19. Frequency sensitivities towards ethanol vapor concentrations of two types of devices – with and without CNT forest.

For the bare device, small frequency shifts are still observed since slight condensation effect may still be occurring despite the increased device temperature. However, at the same temperature, the frequency shifts for the CNT-based device are clearly more pronounced. That is, CNTs improve the sensing performance. In this case, we also note an overall frequency decrease, which means that ethanol molecules are not completely desorbed from the CNT walls by the N₂ cleaning. Binding mechanisms of ethanol, or other specific molecules, to the CNT walls should be studied in depth. To our concern here, we have proven the viability of CNT-based SMRs as vapor sensors. Further studies, including the wide functionalization methods of CNTs to detect more specific targets, is proposed in Chapter 6 as relevant future work.

5.5. Summary

This chapter can be summarized as follows:

- The integration of CNT forest as sensing layers in SMRs was proposed for boosting their gravimetric sensing performance due to the high surface area vertically-aligned CNT offer and their wide chemical affinity. First of all, the problems related to the full integration of CNT forests on SMRs have been addressed. These are the structural resistance of the SMRs at high temperatures (CNT growth requires temperatures higher than 600°C) and the selective growth of CNTs on their metallic top electrodes.
- The mechanical integrity of SMRs at high temperatures has been guaranteed by a specific design, which includes low stressed materials with high interlayer adhesion.

Special emphasis was put on the materials composing the acoustic reflector. Five alternating layers of SiO_2/Mo , with a thin Ti between each pair, proved to be a suitable choice in terms of their similar coefficient of thermal expansion, their high adhesion, the easy control of their residual stress and the high acoustic reflectivity their combination provides. Subsequently, the piezoelectric AlN film was deposited with very low stress by tuning the substrate bias during deposition. This was crucial to avoid delamination due to dilatation effects of all the materials subjected to high thermal gradients.

- Characterization tests of the designed SMRs at up to 700°C demonstrated their high mechanical stability and performance maintenance. Pre and post annealing electrical measurements showed that, when annealed in high vacuum systems, the performance of the device can be even improved owing to the enhancement of the AlN piezoelectricity. Tests in poorer vacuum systems suggested that, when operated in media with high oxygen content, the device should be protected by a capping film to avoid the top electrode (Mo or Ir in this case) oxidation and AlN contamination. The in-situ characterization at high temperatures was also performed, however, in this case the measurement set-up needs to be improved to avoid the parasitic effects the fixtures induce on the devices.
- Regarding the second issue – growth of CNT forests on specific substrates – two different types of substrates were thoroughly studied, namely AlN and metallic films. The direct growth of CNTs on AlN was argued for the use of CNT forest in SMRs as both top electrodes and sensing layers. However, this initial idea evolved to the need of growing the CNTs on the metallic top electrode since the performance of CNTs as electrodes was poor due to high contact resistance. CNT forests with high SWCNT content and high quality were obtained on AlN and metals like Mo and Ir. Key factors to achieve this were the use of an Al under-layer for the Fe catalyst and the temperature used for the nanoparticles formation stage (lower than the CNT growth stage one).
- Subsequently, CNT forests were integrated on SMRs by selectively growing them on the top electrode active area. The influence of the forest on the performance of the device was elucidated. Through electrical measurements before and after CNT integration, it was demonstrated that CNTs have certain degrading influence on the anti-resonance quality factor. This was justified by the poor reflectivity at the top electrode/CNTs interface and the acoustic damping mechanisms inside the forest. It was proved that shorter forests are preferable in terms of electrical performances.
- Finally, a proof of concept on the gravimetric sensing viability of CNT-based SMRs was demonstrated by detecting ethanol vapors.

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Conclusions and future work

This final chapter includes the general conclusions of the thesis and presents possible future lines of investigation based on the obtained results.

6.1. Conclusions

The conclusions of the thesis can be divided in two branches, one related to the results presented in Chapter 4 and another related to the ones from Chapter 5. Regarding Chapter 4, where a 2D FEM model was developed to study the in-liquid sensitivity features of S_0 -LWRs and experimentally verified, we can conclude that:

- The developed model is in good agreement with experiments, being suitable not only for simulating the interaction of S_0 -LWRs with liquids but also that of shear mode FBARs.
- S_0 -LWRs are sensitive not only to the mechanical properties of the liquid (density and viscosity), but also to the electrical properties (dielectric permittivity). In this context two S_0 -LWRs topologies (with and without a bottom electrode) can be used to discriminate between these properties. As an additional advantage, in S_0 -LWRs the liquids under test are dispensed to the device through its backside cavity, leaving the electrodes dry without the need of passivation.
- Within the thin film electroacoustic (TEA) technology, when compared to the widely studied shear mode FBARs for in-liquid operation at the same resonant frequency (900 MHz), S_0 -LWRs are slightly more sensitive to the liquid density viscosity product. Moreover, S_0 -LWRs are more sensitive even when compared to FBARs working at 2

GHz. For all TEA devices sensitivity optimization was proven to be dependent on the device configuration.

- Finally, and most important, S₀-LWRs make use of *c*-oriented AlN films for operation in both, gaseous and liquid media, while for the latter FBARs need tilted AlN films for shear mode operation. Although the shear mode operation in FBARs has been widely studied and optimized, the tilted grains deposition is still a non-industrialized process owing to its poor uniformity. In this context, AlN-based S₀-LWRs can be nowadays the TEA technology with the highest potential for commercialization owing to the mature and industrialized *c*-oriented deposition process and their superior sensing performance.

As for the conclusions of Chapter 5, related to the development of SMRs operable at high temperatures and the integration of CNT forests on SMRs to demonstrate their gravimetric sensing ability, we can state:

- The developed AlN-based SMRs sustaining temperatures as high as 700°C can be considered as a potential alternative to the widely studied LGS-based SAW devices, almost exclusively investigated for this demanding environments. Compared to LGS-based SAW devices, SMRs can bring certain advantages. In contrast to the thin metallic IDTs used in SAW devices, which can suffer from destructive agglomeration problems due to thermally activated electromigration, SMRs use a simple top electrode topology and they allow top electrode thickening for contact resistance reduction, without performance degradation. This can solve the degradation to which metallic thin films are subjected at very high temperatures. Additionally, AlN-based SMRs can work at frequencies of several GHz by simply thinning the layers of the devices, while for SAWs such high frequencies imply using high resolution techniques to reduce the IDT pitch (narrowing the metallic fingers and making them less robust), with the added disadvantage of LGS having increased acoustic losses above 1 GHz.
- SWCNT and MWCNT forest were grown on AlN and some metallic films, like Mo, the material of choice for the SMRs top electrodes. The growth on metallic films was achieved by 1) using a thin Al layer underneath the Fe catalyst, and 2) reducing the nanoparticle formation temperature to 450°C-550°C, as compared to the one used for CNT growth (650°C).
- The successful CNT growth on different substrates, particularly different metallic films like Mo, Ir, W or Ta, can be also used in different applications where the direct growth of CNT on metallic substrates is needed, e.g. VLSI interconnects. The growth

of CNT forest on metallic substrates has been so far one of the most challenging tasks among CNT researchers.

- When integrated on the SMR top electrode, CNT forest induce certain device degradation. This is related to the radiation of part of the acoustic energy to the forest and the wave damping induced the friction between tubes. The taller the forests the higher the degradation induced, which suggests considering a trade-off between device performance and sensing area. Shorter forests (few μm) have proved to degrade less the performance while still providing higher surface area for functionalization.

6.2. Future work

The results reported in this thesis suggest several future lines of investigation. Some of these lines are already running in our group and will be object of future PhD thesis themes. Others, mainly the ones related to LWRs, are more difficult to be continued due to limitations in the fabrication facilities, although other groups with membrane fabrication capabilities are being contacted for collaborations.

As a continuation of the study on the liquid applications of S_0 -LWRs, the suggested future lines of investigation are:

- Application of the studied S_0 -LWRs as biological sensors, that is combining their mass sensitivity features with their in-liquid performance.
- Influence of visco-elastic films, e.g. polymers, deposited on the backside of the AlN membrane as active sensing layers. This can be useful not only for the use of these films as active sensing layers for gas sensing applications, but also to model visco-elastic effects appearing in biological sensors due to possible biochemical layers stacking [1].
- Influence of the conductivity variation in the films or liquids placed on the device backside.
- Experimental verification of the sensitivity optimization predicted in this thesis by FEM modelling. It involves the manufacturing of S_0 -LWRs with different membrane thicknesses.

Regarding the application of SMRs at high temperatures and the integration of CNT forests for boosting their sensing features, the following future lines of investigation are proposed:

- Optimization of the in-situ measurement technique at high temperatures to accurately characterize the performance of SMRs and state the temperature limits of usage. (Already running)
- Development of fully insulating acoustic reflectors sustaining high temperatures. As seen in Chapter 5, this is needed in order to be able to define a bottom electrode for suppressing bonding parasitic effects. Possible high acoustic impedance materials to combine with low impedance SiO_2 can be AlN [2] or Ta_2O_5 [3]. (Already running)
- Extensive gas sensing measurements with different vapors and gases and varied CNT forest properties (height, tube walls, and functionalization) to state their specific sensitivity and resolution.
- Application of SMRs with integrated CNT forests as biological sensors in liquid environments. For that, shear mode operation would be needed, which involves optimization of film stress in tilted AlN layers for high temperature processing. Additionally, the CNT forest needs to be hydrophilic for the liquid to penetrate through the tubes. This requires extensive studies on their proper functionalization not only for inverting their hydrophobic nature but also for detecting specific targets in the liquid. (Already running)
- Detection and isolation of nm-size particles (10-100 nm) is one of the most recent challenges in the biological field. In this context, exosomes have been proven recently to play a key role in intercellular communication, which means they carry valuable information that can be used for clinical prognosis or therapy [4]. Although this has started a growing interest in these particles, their manipulation is still challenging owing to the difficulties arising in their selective isolation and detection [5]. Ultra-centrifugation, micro filtering and chromatography are among the most widely used techniques in the field, although not the most efficient ones. An alternative option for nm-size particles (like exosomes or viruses) filtering has been proposed elsewhere by using CNT forests [6], [7]. In these works they envisaged not only particles filtering but also detection with CNTs. SMRs with integrated CNT forests can be a potential candidates as dual-function devices performing both particles filtering and specific gravimetric detection. The controllable tubes separation in CNT forests can be exploited for size filtering while specific functionalization can be applied for exclusive detection. Experiments on the functionalization of CNT forest have been already initiated with promising results.

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