# *AlN thin film resonators operating at 8 GHz used as sensors for organic films*

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***The mass sensitivity of an AlN thin film resonators operated in air at 6 to 8 GHz has been investigated in theory and experiment. The 30x30 µm wide resonators included a 180 to 300 nm thick, highly oriented AlN thin film, bottom and top electrode, and an acoustic reflector made of AlN/SiO$_2$ multilayers. The top electrode was loaded by defined polymer layers to test sensitivity and simulation model. The impact of type and thickness of the top electrode was simulated. 10 to 20 nm thick PMMA coatings served to demonstrate sensitivity with a gettering gel in form of spontaneous adsorption of acetone from the vapour phase. Finally, a self-assembled monolayer of 11-mercaptoundecanoic acid was formed on a Pt top electrode for the demonstration of a sub-monolayer sensor in air. In both cases, pico-grams could be detected with a sensitivity up to 1000 m$^2$/kg.***

***Gravimetric sensor; Aluminium nitride; Organic films***

## *I.* INTRODUCTION

Gravimetric sensing is a proven technique for the measurement of the mass deposited in thin film deposition, and has a large potential in bio-medical diagnosis to detect mass and viscosity changes resulting from specific bio-chemical processes such as antigen-antibody reactions. The simplest and oldest acoustic wave device is the thickness shear mode resonator made of an AT-cut quartz plate, having its fundamental frequency in the 3-10 MHz range [1]. This device is referred as a quartz crystal microbalance (QCM). Unfortunately, QCM does not offer the required sensitivity for most of the diagnosis mass applications, such as drug screening and medical tests. In the simplest case - considering a bulk wave and assuming the agglomerated material to have the same acoustic impedance as the resonator - the frequency change is proportional to the mass/area ratio $\mu$ of the agglomerated film. Where $v_s$ is the sound velocity in the piezoelectric material, $\rho$ its density, $t_0$ its thickness, $Z_A$ its acoustical impedance and $f_0$ the resonant frequency of the non-coated resonator. From

$$f(\mu) = \frac{v_s}{2}\left(\frac{1}{t_0 + \mu/\rho}\right) \qquad (1)$$

The frequency shift per agglomerated mass density μ is calculated as

$$S_a = \lim_{\mu \to 0} \frac{\Delta f}{\mu} = -\frac{v_s}{2\rho}\left(\frac{1}{t_0}\right)^2 = -\frac{2}{v_s \rho} f_0^2 = -\frac{2}{Z_A} f_0^2 \qquad (2)$$

where $S_a$ means the sensitivity measured in an absolute frequency shift. This one increases as $f_0^2$, meaning a tremendous increase in sensitivity with frequency. In practice one considers rather the relative frequency shift $\Delta f/f_0$ as relevant for the sensitivity, thus defined $S_r$ as [2]:

$$S_r = \frac{1}{f_0} \lim_{\mu \to 0} \frac{\Delta f}{\mu} \qquad (3)$$

## *II.* *EXPERIMENTAL*

The resonators are fabricated using technology described in [3-5]. A schematic view of the resonators is given on the figure 1.

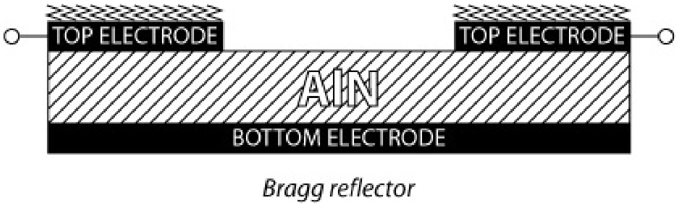

Figure 1. Schematic cross section of the resonators loaded with an organic layer.

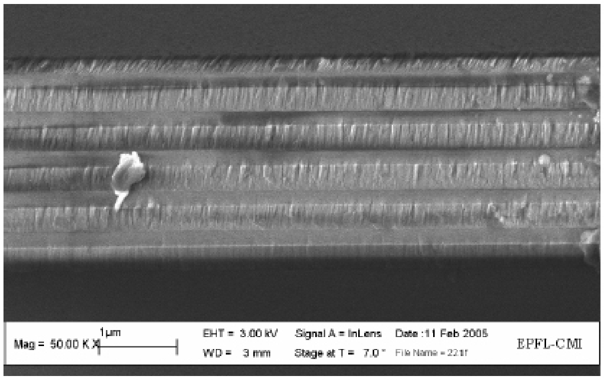

Figure 2. SEM micrograph of the Bragg reflector.

Two different types of resonators were used during theses experiments one with an aluminium top electrode noted as Al-type and one with a platinum top electrode noted as Pt-type. Their characteristics are given in the Table 1. The Q factors are defined and measured as in [6].

Table 1: Description of the two resonators used for experimental testing

| | *Bottom electrode* | *Piezoelectric AlN film* | *Top electrode* | *Q* |
|---|---|---|---|---|
| Al-Type | Pt, 100nm | AlN, 300nm | Al, 100nm | 200 |
| Pt-type | Pt, 100 nm | AlN, 180nm | Pt, 60nm | 350 |

For mass loading testing, 3-15 nm thickness range polymer films (S1813 resist Shipley) were obtained by dilution in acetone. The solution is subsequently spinned on the devices at 2000 rpm for 20s and baked for 60s at 115°C on a hotplate. The thickness of the polymer layers was then measured by a profilometer (Tencor). The complex admittance of the resonators was measured with a Vector Network Analyser (Hewlett Packard, 8722D).

## *III.* RESULTS AND DISCUSSION

The resonators are simulated using the general one-dimensional treatment from Nowotny and Benes [7] providing a solution for the four differential equations from the linear theory of piezoelectricity with the hypothesis of a quasi static electrical field.

$$c_{ijkl}\frac{\partial^2 u_k}{\partial x_i \partial x_l} + e_{mij}\frac{\partial^2 \phi}{\partial x_m \partial x_i} = \rho \ddot{u}_j \qquad (4)$$

$$e_{lnk}\frac{\partial^2 u_k}{\partial x_l \partial x_n} - \varepsilon_{rs}\frac{\partial^2 \phi}{\partial x_r \partial x_s} = 0 \qquad (5)$$

Each layer is described by the following properties: the density $\rho$, the thickness $t$, the elastic stiffness constants $c_{ijkl}$, the dielectric constants $\varepsilon_{ij}$ and the piezoelectric constants $e_{ijk}$. $U$ is the displacement vector and $\phi^2$ the electrical potential. The number of layers is unlimited but the number of electrodes must be equal to 2. The materials parameters used for the simulations are given into the Table 2.

Table 2 : Properties of the simulated materials, [a] the dielectric constant must by multiplied by $\varepsilon_0$, [b] stiffness is supposed to be isotropic

| | $\rho$ *(kg/m³)* | $\varepsilon^a$ | $c_{11}$ *(GPa)* | $c_{12}$ *(GPa)* | $c_{44}$ *(GPa)* | $e_{33}$ *(Cm⁻²)* | $e_{31}$ *(Cm⁻²)* | $e_{15}$ *(Cm⁻²)* |
|---|---|---|---|---|---|---|---|---|
| Pt | 21500 | - | 0.347 | 0.251 | 0.077 | - | - | - |
| Al | 2700 | - | 0.107 | 0.06 | 0.03 | - | - | - |
| AlN | 3260 | 10.5 | 0.42 | 0.14 | 0.14 | 1.55 | -0.58 | -0.48 |
| $SiO_2$ | 2200 | 4 | 0.074[b] | - | - | - | - | - |
| Photoresist | 1180 | 5 | 0.008[b] | - | - | - | - | - |

This model allows to plot the sensitivity $S$ in $m^2kg^{-1}$ of each type of resonator with the dimensionless parameter $z = t\, f_0/v_P$. Where $t$ is the thickness of the polymer layer added and $v_P$ the sound velocity in this layer.

In order to maximise sensitivity $S$, different types of resonators were simulated (figure 3). The Al-type resonator was optimized changing only the nature and the thickness of the top electrode. $S_r$ increases with the thickness of the Al electrode (curves 1 and 2). It is assumed that the sound velocity in polymer $v_P$ equals 1200 m/s and that the its density equals 1180 kg/m³. The model also shows that the addition of an impedance matching layer of $SiO_2$ on the Al top electrode increases the sensibility of the resonator (curve 3).

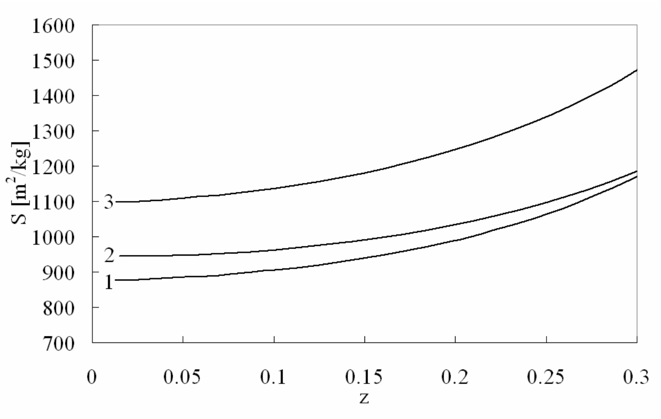

Figure 3. Simulated sensitivities in m$^2$/kg are plotted in function of $z=(t\ x\ f_0)/v_P$ for the Al(100nm)/AlN(300nm)/Pt(100nm) resonator (curve 1), Al(200nm)/AlN(300nm)/Pt(100nm) resonator (curve 2) and $SiO_2$(20nm)/Al(80nm)/AlN(300nm)/Pt(100nm) resonator (curve 3).

The Al-type resonator used for experiments in this work had an electrode thickness of 100 nm. The sensitivity can be increased using thicker Al films (200 nm simulated for curve 2) to $S_r$=945 m$^2$/kg (or $S_a$=9450 Hz x cm$^2$/ng), however, the frequency drops considerably to 5.9 GHz. Better improvements are realized by adding a 20 nm layer of $SiO_2$ on an 80 nm aluminium top electrode (curve 3). This structure enhances sensitivity by 20 %. The transmitted part of the wave in the polymer increases due to the smaller acoustic impedance of the $SiO_2$ and improves the sensitivity $S_r$ to 1100 m$^2$/kg (or $S_a$ 11000 Hz x cm$^2$/ng). The two types of resonators fabricated were also simulated with an increasing thickness of the polymer layer on the top electrode. The simulated $S_r$ is increasing with $z$ (see figure 3). $S_r$ is four times greater for the Al-type (875 m$^2$/kg) than for the Pt-type (222 m$^2$/kg). The *S(z)* curves also allow the validation of the simulation model. Some experimental measurements with polymer layers onto the top electrode of the resonators were carried out. These measurements are presented with the simulated curves of the Al and Pt type resonators on the figure 4. The errors bars are calculated based on the inaccuracy of the thickness measurement and amount to 5% to 7% using Al-electrodes, and 1% to 8% using Pt electrodes. Experiment and simulation agree very well.

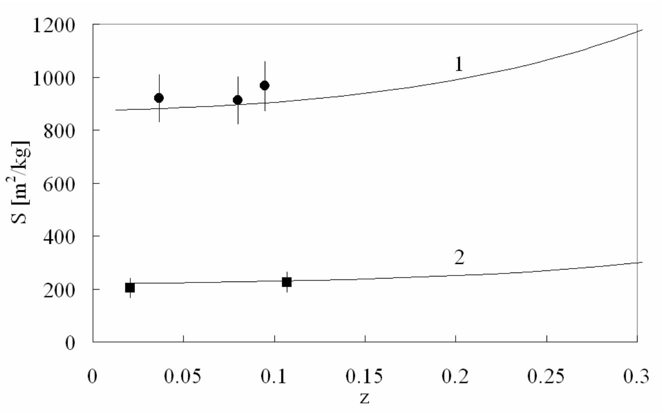

Figure 4. Correlation between simulated sensitivities (lines) and experimental measurements (points) for the Al(100nm)/AlN(300nm)/ Pt(100nm) (1) and Pt(60nm)/AlN(180nm)/Pt(100nm) (2) resonators. The sensitivities in m$^2$/kg are plotted in function of $z = t\,f_0/v_P$.

11-Mercaptoundecanoic acid is a molecule well known to form self assembled monolayers on noble metal surfaces. In our work we use the platinum top electrode as attachment surface. The monolayer is obtained by dipping a Pt-type resonator in a solution $5x10^{-3}$M of 11-mercaptoundecanoic acid in tetrahydrofuran (THF). The resonant frequency shift due to the mass of acid deposited on the electrode of the Pt-type resonator is 6 MHz. The quality factor drops from 183 to 177, but is still sufficiently large for high- resolution detection.

The adhesion of the organic molecules was confirmed by XPS measurement of the carbon 1s peak. The concentrations of carbon on the SAM loaded resonator (14400 cps) significantly larger than on a bare resonator (9400 cps) [8].

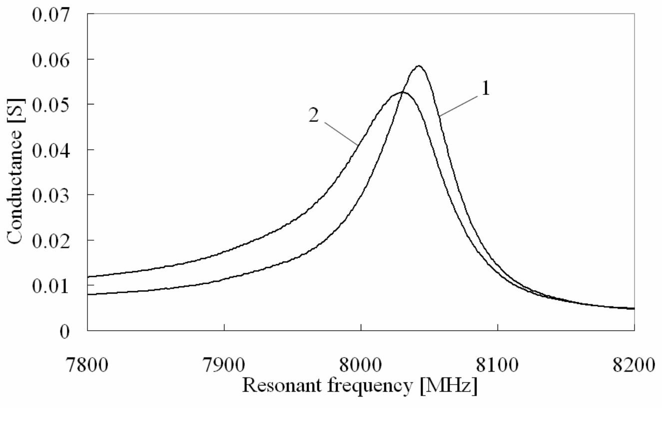

Figure 5. Frequency spectra of the conductance for the Pt(60nm)/AlN(180nm)/Pt(100nm) resonator. The spectrum (1) is made with an uncoated resonator and the spectrum (2) with a resonator covered with a layer of 11-Mercaptoundecanoic acid.

The measured sensitivity for this type of sensor equals 200 $m^2$/kg assuming a dense arrangement of the molecules. The calculated frequency shift corresponds to a load of a 2 nm layer of PMMA. This value corresponds well to the length of the molecule of 11-Mercaptoundecanoic acid, and thus confirms that the assumed density is about correct. With the high quality factor it is possible to detect frequency shift of 1 MHz and to achieve a mass resolution of nano grams per square centimetres, even though the Pt-type sensitivity is not the best of the resonators tested. Assuming the rigidity to be similar to the one of PMMA, the total detected mass is calculated as 2 pg. Considering the 1 MHz resolution of the measurement, one arrives at a resolution of 0.4 pg. A potential error in rigidity does not modify this result substantially. According to simulation, a reduction of stiffness by a factor 10 increases sensitivity by a factor 3/2 only.

A 20 nm uncured polymer layer on the Al top electrode serves as selective coating for the detection of vapour phase acetone. The porosity of the uncured polymer layer promotes acetone molecules absorption. The resonator was surrounded by a box containing a saturated atmosphere of acetone (233 mbar) and exposed during 50s, after which the box was removed. The admittance was measured every 5s. The resulting resonance frequencies are depicted in figure 6. In the absorption phase, $f_R$ progressively decreases before stabilizing after 40 s. When the sensor is removed from the acetone atmosphere the $f_R$ rapidly increase and returns to the former level.

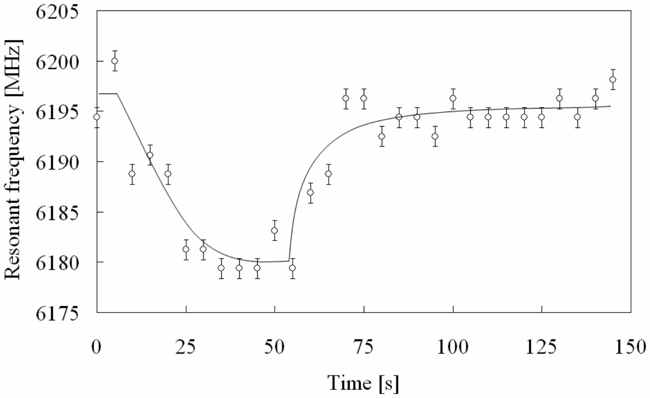

Figure 6. Resonant frequency change during time of the polymer coated Al(100nm)/AlN(300nm)/Pt(100nm) resonator. For the first 50s, the resonator is exposed to an atmosphere of acetone and then to the air.

The hypothesis is made that the resonant frequency shift is only due to the density variation caused by the adjunction of mass in the volume of the polymer film. The simulation shows that the sensitivity for density changes $\Delta f/\rho$ amounts to 0.2 MHz$m^3$/kg for the Al-type resonator. The experimental shift of 15 MHz between the unsaturated and saturated polymer layer corresponds to a density change of 75 kg/$m^3$, meaning a 6 % increase with respect to the PMMA density. For a constant volume of the polymer layer (30 µm x 30 µm x 20 nm) this density corresponds to a mass of 1.35 pg. Fixing the dimensions and increasing the density of the polymer layer, $S_r$ equals 1250 $m^2$/kg.

The increase with frequency is very evident. Thin film BAW's have the further advantage of a small surface, allowing for low production costs and array fabrication. In addition, the small amount of mass required for the detection is a great advantage for biosensors.

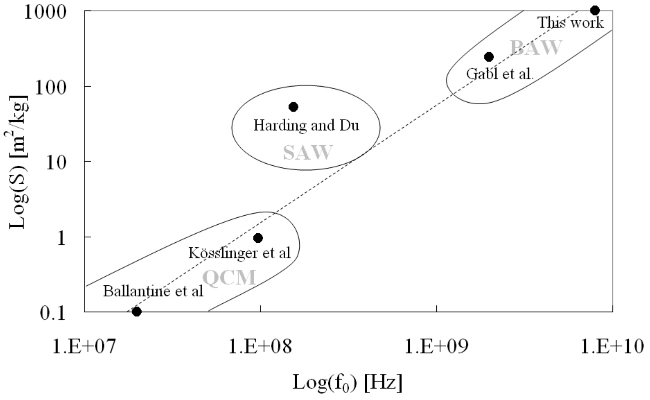

Figure 7. Summary of the sensitivities *S* for different types of resonators according to their resonant frequencies $f_0$. Ballantine refers to [1], Kösslinger to [9], Harding to [10] and Gabl to [11].

## IV. SUMMARY AND CONCLUSION

8 GHz gravimetric sensors based on AlN Solidly Mounted Resonators have been used as sensors for detection of polymer layers, acetone vapour and 11-Mercaptoundecanoic acid molecules. The high working frequency resonators have demonstrated an evident increase in sensitivity compared to QCM but also compared to 2 GHz ZnO Bulk Acoustic Wave resonators [11]. The observed relative sensitivity $S_r$ increases linearly if not faster with frequency. Using Al top electrodes directly as layer to which organics attach, a sensitivity of $S_r$= 900 m$^2$/kg is calculated and confirmed by experiments with PMMA thin films. Within the validated model, an improvement of sensitivity to $S_r$= 1100 m2/kg is predicted using a thin $SiO_2$ matching layer. Pt is an ideal layer for working with self assembled thiol mono-layers. However, the sensitivity drops to 200 m$^2$/kg, for the acoustic coupling to organics is weak. Nevertheless, the sensor is able to detect a monolayer of 11-mercaptoundecanoic acid with a very significant frequency shift of 6 MHz. The sensor can be used to detect agglomerated mass as well as mass and stiffness modifications of a sensor layer absorbing gases or vapours. The absorption of acetone vapour in PMMA showed that the resonators can detect less than one pg on electrode of 900 μm$^2$, corresponding to a sensitivity $S_r$ 25% larger than as gravimetric sensor. Theses results let expect a very promising future for devices coated with a specific gel capable of absorbing selectively specific molecules.

## ACKNOWLEDGMENTS

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