

Carbon nanotube isolation layer enhancing in-liquid quality-factors of thin film bulk acoustic wave resonators for gravimetric sensing

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Abstract

A thickness longitudinal mode (TLM) thin film bulk acoustic resonator biosensor is demonstrated to operate in water with a high quality-factor, Q . This is achieved using a layer of carbon nanotubes (CNTs) on top of the resonator which has a significantly different acoustic impedance to either the resonator or liquid whilst being susceptible to the binding of biological molecules. This allows the resonance to be decoupled from direct energy loss into the liquid, although still retaining mass sensitivity. AlN solidly mounted resonators (SMRs) having a thickness shear mode (TSM) at 1.1 GHz and TLM at 1.9 GHz are fabricated. CNTs with different forest densities are grown by chemical vapor deposition on the active area with Fe as catalyst and resulting devices compared. High forest density CNTs are shown to acoustically decouple the SMRs from the water and in-liquid TLM Q values higher than 150 are recorded even exceeding TSM SMRs without CNTs. The TLM Q in water is remarkably improved from 3 to 160

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for the first time by dense CNT forests, rendering the large-scale fabrication of TLM SMRs for liquid-phase sensing applications possible. Despite this partial isolation, SMRs with CNT forests $\sim 15 \mu\text{m}$ tall can still detect binding of bovine serum albumin.

Keywords: Carbon nanotubes, Bulk wave resonators, Gravimetric sensing, Acoustic wave decoupling, In-liquid sensors

1. Introduction

In recent years the need for miniature, low cost, label-free and ultra-sensitive chemical and biological sensors has grown significantly. Gravimetric sensors based on acoustic wave resonators, which have been predominantly used in
5 r.f. filters, are ideal to achieve these objectives. Mass accretion on the sensor surface (which can be functionalized to only permit specific molecules to attach) decreases the resonant frequency, f_r ; this is the basis for sensing. This frequency shift, Δf_r , and hence the mass sensitivity, S_m , are proportional to f_r^2 according to the Sauerbrey equation [1]. Better mass sensitivities are there-
10 fore achievable by operating at higher frequencies. Acoustic wave resonators can be broadly categorised into surface acoustic wave (SAW) and bulk acoustic wave (BAW) resonators. SAWs are generated on a piezoelectric material by applying an electrical signal to a set of interleaved electrodes known as interdigitated transducers (IDTs), which are a comb-like array [2]. Typically SAWs
15 are guided along the free surface and decay exponentially with depth ($> 90\%$ within one wavelength from surface) while BAWs propagate freely like in an infinite medium [3]. Higher f_r through miniaturisation of IDTs in SAW resonators is difficult to achieve due to lithography constraints [4]. In addition, at higher f_r , SAW resonators have lower Q -factors and limited power handling
20 capabilities [5], although the mass sensitivity has been shown to improve when increasing the operating frequency from 80 MHz to 1 GHz [6]. Quartz crystal microbalances (QCMs) are the most well-established BAW gravimetric sensors; these use quartz plates ($330\text{-}55 \mu\text{m}$ thick) and operate generally in a shear mode

with frequency (5-20 MHz) [7, 8]. To increase the f_r , expensive processes are
25 necessary to thin the quartz plates, which eventually become fragile. However
higher frequency (1-5 GHz) resonators have been amenable by thin film tech-
nology, through the emergence of thin film BAW resonators.

Thin film BAW resonators generally consist of a thin piezoelectric film (0.5-3
 μm thick) of aluminium nitride (AlN) or zinc oxide (ZnO) “sandwiched” between
30 two metallic electrodes [9]. The application of an a.c. signal across the electrodes
generates a standing wave confined in the piezoelectric layer, which resonates
at a frequency that is determined by the film thickness [10]. Depending on the
method of isolating the acoustic wave from the substrate, two types of BAW
resonators can be distinguished: film bulk acoustic resonators (FBARs) and
35 solidly mounted resonators (SMRs). FBARs use air for acoustic isolation; SMRs
have an acoustic reflector consisting of layers alternating between low acoustic
impedance and high acoustic impedance [9]. Thin film BAW resonators are
normally operated in the thickness longitudinal mode (TLM), which is excited in
piezoelectric films with a c -axis oriented parallel to the resonator surface normal.
40 Thus the application of an r.f. signal causes the mechanical deformation to be
parallel to the direction of wave propagation [11]. Biosensing with longitudinal
mode thin film BAW resonators is usually performed in dry conditions as the
TLM couples efficiently into liquids leading to severe damping ($> 90\%$ drop in
quality-factors at resonance, Q) [12]. This prevents TLM resonators from being
45 used in liquid environments, which is a major hindrance for both chemical and
biological sensing as it requires surfaces to be dry when measurement takes
place. Thus far the thickness shear mode (TSM) resonance has been adopted
for biosensing applications because it does not compress in liquids with low
viscosity and hence has lower attenuation [13].

50 In-liquid TSM resonators in the GHz regime have already been shown in
the real-time measurement of antibody-antigen binding [14], study of DNA hy-
bridization [15, 16] and organophosphorus pesticide detection [17]. TSM reso-
nances can be excited effectively by using a piezoelectric layer with a c -axis in-
clined between 20° – 40° with respect to the surface normal, and this is achieved

55 by an off-axis growth of the film as reported in [18, 19, 20, 21]. Both the TSM
 and the TLM are stimulated (quasi-shear and quasi-longitudinal modes) in such
 piezoelectric films, with the TSM resonating at a lower frequency compared with
 the TLM because of the lower propagating velocity of the shear wave. Due to
 this lower f_r , the mass sensitivity of the TSM is only around one-third of the
 60 corresponding parameter for TLM resonators having similar dimensions [14].
 In addition, damping still occurs when the shear resonance propagates through
 more viscous liquids [12, 22]. Crucially, the scalability of fabricating inclined
c-axis films is also limited compared to highly oriented *c*-axis films due to sig-
 nificant and expensive modifications necessary for the depositions as reported
 65 in previous works [23, 24]. Alternative methods using either seed layers such
 as AlN [19, 12] with specific crystallographic orientations or Al electrodes with
 controlled roughness [25] improve the uniformity of inclined *c*-axis piezoelectric
 films over a short range but still cannot achieve homogeneity over larger sub-
 strates. It would therefore be preferable to find a means of using the TLM for
 70 in-liquid sensing. Attempts to confine the liquid using microchannels have been
 attempted to reduce damping in the TLM [26, 27]. However the attenuation of
 the TLM is very sensitive to the channel thickness, which needs to be precise
 to prevent large energy loss into the liquid [26]. The second harmonic of the
 TLM has also been reported for in-liquid sensing, although at higher f_r , low Q
 75 of 40 are achieved, which reduces the measurement accuracy of Δf_r and hence
 S_m [28]. Pottigari and Kwon [29] designed FBARs with a vacuum gap to isolate
 the resonator from liquid interaction by using a parylene membrane held by
 microposts. Even though the measured in-liquid Q was ~ 140 , the area of the
 resonator in contact with vacuum forms a parallel resonator with the area under
 80 the posts, which significantly reduces the sensitivity to mass variations on the
 membrane. The fragility of such a device also limits its potential for in-liquid
 TLM thin film BAW sensors.

In this work, a new approach using an interface layer between the resonator
 and the liquid to enable TLM devices for working in-liquid is presented. Rather
 85 than isolating the resonator entirely from the liquid, the purpose of this layer

is to partially isolate the TLM and TSM from the liquid by engineering the thickness of this interface layer. In addition the interface layer itself can be functionalized to allow mass attachment (from molecules in the liquid), which is detected by the resonant acoustic wave. In this way, the interface layer decouples
90 the resonant device from the process of mass attachment whilst retaining mass sensitivity in the liquid. This is demonstrated using a layer of carbon nanotubes (CNTs), which is grown directly on the active area of the resonator.

Owing to their extraordinary electronic and mechanical properties (stiffness coefficient ~ 1 TPa, acoustic velocity ~ 62 km \cdot s $^{-1}$) [30, 31], CNTs have tremendous potential for application in gravimetric biosensors. In addition to their
95 compatibility and affinity to biological compounds [32], the larger surface area to volume ratio of CNTs makes them an attractive alternative to metallic electrodes for improving the sensitivities and detection limits of thin film BAW biosensors. Indeed CNT integration on the surface increases the binding area
100 for molecules without physically increasing the dimensions of the sensor. Consequently, for the same concentration of a biological sample, a larger number of targeted molecules can be bound onto the resonator surface compared to devices with metal electrodes; both ZnO [33] and AlN [34] thin film BAW resonators with higher sensitivities attributed to the presence of a CNT layer have already
105 been demonstrated in air using the TLM.

When the CNTs are grown directly on substrates, they form different morphologies depending on their number density. With number densities as high as $\sim 10^{11}$ – 10^{13} cm $^{-2}$, the growth of vertically-aligned (VA) CNT forests is favored [35]. Although in this work only the forest number density will be
110 considered, the low mass densities of CNT forests ranging from 0.03 g \cdot cm $^{-3}$ (Futaba *et al.* [36]) to 1.6 g \cdot cm $^{-3}$ (Sugime *et al.* [37]) effectively reduce mass loading on the resonators compared to metal electrodes. Depending on their morphology, CNTs can have different acoustic impedances, which can be tuned to ensure a sufficient mismatch with the acoustic impedance of the piezoelectric
115 material to confine the acoustic wave in the resonator [31, 38]. CNTs have a further merit compared to metals as they can be functionalized for direct cova-

lent bonding to molecules, or for non-covalent bondings by means of different types of polymers [39] thus preventing non-specific binding or the need for additional binding layers. Moreover the chemical bonding structure of CNTs, which
120 consists of carbon atoms only, is attractive for detecting organic compounds. Hence, the potential exists to use functionalized CNT layers, which would function both as electrodes and as sensing layers [40]; however electrodes made only with CNTs introduce parasitic series resistances, which deteriorate the Q -factor values at resonance in air according to [41].

125 To assess the viability of CNTs functioning as an interface layer, inclined c -axis AlN based SMRs operating at fundamental TSM and TLM frequencies of ~ 1 GHz and of ~ 2 GHz respectively are fabricated. The CNTs are grown by chemical vapor deposition (CVD) on the active area so that they act solely as an acoustic decoupling layer to mitigate acoustic energy loss in a liquid environment. The impact of this CNT layer on the TSM and TLM resonances are
130 investigated and compared to resonators without a CNT layer. Three different CNT forest densities are investigated ranging from densely-packed CNT forests to “spaghetti”-like tubes. Additionally the mass sensitivities in liquid of CNT coated SMRs are also evaluated.

135 2. Material and methods

The SMRs shown schematically in Figure 1 (a) are fabricated on (100)-oriented, n -type, $500\ \mu\text{m}$ thick Si wafers with diameter 100 mm, which have been thermally oxidized (wet-oxidation) to obtain ~ 620 nm of SiO_2 . Four reflector layers consisting of alternating Mo (~ 650 nm) and SiO_2 (~ 620 nm) are
140 then sputtered sequentially in a Leybold Z500 sputtering system to achieve a reflection centered around a frequency of 2.2 GHz for the longitudinal mode. The top reflector layer is polished mechanically using alumina slurry to reduce the roughness to less than 2 nm. Ti/Ir ($\sim 20/130$ nm) is deposited as a bottom electrode by electron beam evaporation and 400 nm of Mo is deposited
145 by sputtering as a hard mask. With standard UV photolithography this hard

mask of Mo is patterned and etched by commercial aluminium etchant. The exposed Ir is then etched by Ar ion-milling followed by dry etching of Ti with SF₆ chemistry to define the bottom electrode. Subsequently the Mo hard mask is removed by commercial Al etchant. AlN sputtering is performed in an in-house
150 ultra-high-vacuum system, pumped to a base pressure below 8×10^{-7} Pa. A pulsed DC source (MKS ENI 235, Andover, MA, USA) operating at 250 kHz powers a high purity (99.999%), 150 mm diameter Al target. An AlN seed layer (~ 100 nm thick) is grown prior to the piezoelectric AlN, at high pressure (0.66 Pa) and 600 W without intentionally heating or biasing the substrate. With
155 these conditions seed layers with mainly (103) orientation are deposited, which are essential to promote the growth of the subsequent AlN films with inclined grains as shown in Figure 1 (c) [19]. AlN films with the wurtzite *c*-axis inclined up to 24° (Figure 1 (c)) with respect to the surface normal in the substrates placed between 2 and 5 cm from the target axis. The piezoelectric AlN films
160 (~ 1 - $1.2 \mu\text{m}$ thick) are sputtered at lower pressure (0.27 Pa, in a 60% N₂ in Ar admixture), maintaining the substrate at 550 °C and applying r.f. bias of -50 V to keep the residual stress below 200 MPa. The top electrode of Mo (~ 150 nm) is sputtered in a DC magnetron sputtering system (Metallifier Sputter Coater, Precision Atomics, Cambridge, UK) from a 99.95% Mo target at a power of 100
165 W in a 0.35 Pa Ar atmosphere. This top electrode is then patterned by standard UV photolithography and dry etched with reactive ion etching using CF₄/O₂ chemistry. For the devices with CNTs, the active area (a pentagon inscribed in an $80 \mu\text{m}$ diameter circle, Figure 1 (b) forming an active area of 1.42×10^{-4} cm²) is defined using standard UV photolithography. Al (8 nm thick) and Fe
170 (thickness ranging from 0.5 nm to 4.5 nm) are deposited in a thermal evaporator (E306, Edwards, West Sussex, UK) at a base pressure of 2×10^{-4} Pa, and the samples are exposed to air after Al evaporation [42, 43].

Multi-walled CNTs are grown on the devices by CVD method in a cold wall chamber (Black Magic, Aixtron SE, Herzogenrath, Germany) according
175 to the schematic process shown in Figure 2. The substrates are loaded in the chamber, which is then evacuated to a base pressure of 6.0 Pa with a rotary

pump. Ammonia (NH_3) is introduced at a rate of 100 sccm in the chamber to raise the pressure to 16 Pa and stabilized for 30 s. NH_3 is chosen as a reducing gas since it is more efficient than H_2 to reduce catalyst particles to its metallic state especially at low temperature [44]. The substrate is subsequently heated up from room temperature to the growth temperature (ranging from 450 °C to 650 °C) at a rate of 3 °C·s⁻¹ and stabilized for 300 s. This ramping rate is chosen as a compromise to prevent delamination of the layers while avoiding Oswald ripening of the catalyst. Upon heating, the Fe catalyst is reduced and dewets to form nanoislands and by varying the thickness of Fe (from 0.5 nm to 4.5 nm), different sizes of nanoislands are formed leading to CNTs with different densities and thicknesses. After the annealing step, the carbon feedstock, acetylene (C_2H_2), is added to commence growth. The ratio of NH_3 and C_2H_2 is 1:1 to prevent the deposition of amorphous carbon during the growth, which is carried out at a pressure of 32 Pa. After the growth time has elapsed, the heater is turned off, C_2H_2 and NH_3 are switched off before flowing Ar (200 sccm) until the system cooled down to room temperature as shown in Figure 2. Attempts were also made with ZnO as a piezoelectric material, however the ZnO film reacted with NH_3 and is reduced to Zn. A passivation layer that withstand the annealing step is therefore necessary to protect ZnO for CNT growth on the active area.

The CNTs are characterized using field emission scanning electron microscopy (FE-SEM) (LEO 1530VP scanning electron microscope, LEO electron microscopy Inc, New York, USA) using an acceleration voltage ranging from 0.5 keV to 5 keV. Cross-sections of cleaved samples, onto which the CNT forests have been grown, are analyzed to assess the height and forest density of the CNT layer in more detail. Area densities of the CNT forests are estimated by determining the average number of tubes across five sets of regions with 2 μm distances from the SEM cross-sectional images and projecting to an approximate number of tubes over a 1 cm^2 area. The CNT chemical structures are assessed by Raman spectroscopy (inVia confocal Raman microscope, Renishaw plc, Gloucestershire, UK) using a 532 nm wavelength laser. The scan range is chosen to be from 1000

cm^{-1} to 3500 cm^{-1} as there were no peaks at lower wavenumbers to suggest the presence of single wall CNTs.

210 The electro-acoustic responses of the SMRs are characterized on a coplanar probe station using ground-signal-ground (G-S-G) probes with $150 \mu\text{m}$ pitch (Picoprobes, GGB industries Inc., Naples, FL, USA). A network analyzer (Model E5062A, Keysight Technologies, Santa Rosa, CA, USA) is used to measure the frequency response of the devices from 0.5 to 3.0 GHz. The frequency corresponding to the maximum of the real part of the electrical admittance, Y , is
 215 considered as f_r and the frequency corresponding to the maximum of the real part of the electrical impedance, Z is considered as f_a . To assess the resonator performance the Q value at resonance and effective electromechanical coupling, k_{eff}^2 , coefficient are determined from standard definitions given by equations (1) and (2) [45].
 220

$$Q = \frac{f_r}{2} \left| \frac{d\Phi_Y}{df} \right|_{f=f_r} \quad (1)$$

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

where Φ_Y is the phase of Y .

In-liquid Q -factors and Y spectra of both CNT coated and non-CNT SMRs are measured by carefully dropping $50 \mu\text{L}$ of de-ionized (DI) water using a micropipette on top of the active area. To investigate the mass sensing ability of
 225 the SMRs, bovine serum albumin (BSA) is chosen due to its water solubility and high affinity to CNTs, which enable its adsorption on the forest. BSA solution in water with a concentration of $20 \text{ mg}\cdot\text{mL}^{-1}$ (B86657-5 mL) is purchased from Sigma Aldrich Ltd, which is then diluted with DI water to produce three different concentrations of BSA solutions: $50 \mu\text{g}\cdot\text{mL}^{-1}$ (1:399 BSA:DI water), 1000
 230 $\mu\text{g}\cdot\text{mL}^{-1}$ (1:19 BSA:DI water) and $2500 \mu\text{g}/\text{mL}$ (1:7 BSA:DI water). Pure DI water is initially dropped each device tested to obtain the reference value of f_r for no BSA binding. The DI water around the device is then carefully adsorbed using clean wipes, before allowing the device to dry for 5 mins. $50 \mu\text{L}$ of one of the three concentrations of BSA solution is dropped by means of a micropipette

235 on the SMRs covering the G-S-G probe as well and the Y spectra are recorded
at 2 min intervals to allow the BSA to bind to the CNT. Typically the shifts
in f_r caused by BSA attachment stabilized after 5 mins. The responses to DI
water and subsequently BSA for the remaining concentrations are then repeated
on an SMR with CNT that has not been exposed to BSA.

240 **3. Results and discussion**

3.1. CNT characterization with different catalyst thickness

SEM images shown in Figure 3 (a) (i) and (ii) illustrate the different forest
heights and densities obtained with Fe catalyst thicknesses from 0.5 nm to 4.5
nm, as it is known that catalyst thickness significantly influences CNT mor-
245 phology [46]. In Figure 3 (a) (i), inclined images of the forest on top of the
electrode are shown, whereas in Figure 3 (a) (ii), the cross-sectional cut of the
forests grown on Si wafers are depicted. From the SEM images, it is observed
that when the thickness of the Fe catalyst is decreased from 4.5 nm to 0.5 nm
the forest height increases from $< 1 \mu\text{m}$ to approximately $\sim 15 \mu\text{m}$ for the same
250 growth time of 3 minutes. In addition, a thinner catalyst layer causes the CNT
forests to become more packed; hence their area density increases, as smaller
nanoparticles (NPs) are formed and the individual tubes are closer to one an-
other leading to tall VA-CNTs [47]. In contrast with Fe thicknesses of 4.5 nm,
the CNT layer tends to be more “spaghetti”-like with random orientations and
255 a lower area density, which are not ideal for biosensing. The optimum tempera-
ture to activate the Fe catalyst for the growth and to reduce delamination of the
SMR reflector layers is found to be at 600 °C; lower temperatures either caused
slower growth rate or no growth. Higher temperatures, which could improve
the CNT quality, are detrimental to the integrity of the devices as the different
260 thermal expansion coefficients of the materials in the SMR stack lead to stress
and eventually delamination. Similarly a compromise heating rate of rise of 3
°C·s⁻¹ is chosen to allow NP formation and avoid film delamination during the
annealing step in Stage 1. At 600 °C, the growth rates are found to be approx-

imately $5 \mu\text{m}\cdot\text{min}^{-1}$, $3 \mu\text{m}\cdot\text{min}^{-1}$ and $0.2 \mu\text{m}\cdot\text{min}^{-1}$ for Fe thicknesses of 0.5
 265 nm, 1.5 nm and 4.5 nm respectively as shown in Figure 3 (a) (ii). From the
 cross-sectional SEM micrographs, estimates for the area densities of the CNT
 forests are obtained as $\sim 0.3 \times 10^{10} \text{ cm}^{-2}$ denoted as the low density (LD) CNTs
 with 4.5 nm Fe, $\sim 1.4 \times 10^{10} \text{ cm}^{-2}$ corresponding to medium density (MD) CNTs
 with 1.5 nm Fe, and $\sim 2.2 \times 10^{10} \text{ cm}^{-2}$ for high density (HD) CNTs with 0.5
 270 nm Fe. Optical microscope (OM) images shown in Figure 3 (a) (iii) confirm
 the presence of the CNT forests on the active area of the SMRs. Shorter CNT
 forests are in focus with the resonator surface as in the case with 4.5 nm Fe,
 whereas taller CNTs are out of the focal plane in the case of 0.5 nm Fe and 1.5
 nm Fe. Additionally a clear change in the transparency of the active area of the
 275 SMRs can be observed from the dense CNT forests to the lowest density CNT
 layer, indicating the reduced CNT packing with thicker Fe layers. The Raman
 spectra displayed in Figure 3 (b) show the presence of both a G -peak at 1583 cm^{-1}
 and a D -peak at 1350 cm^{-1} , which are typical for multi-wall CNTs in the
 different CNT morphologies investigated as reported in [43]. The intensity ratio
 280 of the G -peak to the D -peak (I_G/I_D) of 1.1 with 0.5 nm Fe can be explained by
 a slightly reduced disorder in the CNT forest [48]. With 1.5 nm Fe the intensity
 of the D -peak becomes higher than its corresponding value for the G -peak in-
 dicating the deterioration of crystallinity of the CNT. Likewise with 4.5 nm Fe
 the ratio I_G/I_D is further reduced to 0.84, hence confirming lower crystallinity
 285 in the CNTs grown with a thicker Fe layer.

3.2. Electro-acoustic characterization of SMRs in air and DI water

The measured $Y(S)$ spectra of the SMRs fabricated with and without CNTs
 are shown in Figure 4 (a). Both a TSM ($\sim 1.1 \text{ GHz}$) and a TLM ($\sim 1.9 \text{ GHz}$)
 resonance are observed in the spectra with a spurious resonance of smaller am-
 290 plitude at $\sim 1.6 \text{ GHz}$ (Figure 4 (a)). This spurious resonance is caused by larger
 thicknesses in the reflector layers to compensate for temperature coefficients of
 frequency [49], which lead to overtones in the frequency spectra. Inclinations of
 the AlN grains caused by the off-axis deposition ($\sim 24^\circ$, shown in Figure 1 (c))

lead to these quasi-shear and quasi-longitudinal resonances. These TSM and
 295 TLM resonances of the SMRs (average of ten representative devices, and stan-
 dard deviation as errors) are obtained at frequencies of (1.13 ± 0.05) GHz and
 (1.94 ± 0.07) GHz respectively as shown in Figure 4 (a). Comparatively, devices
 with CNT forests on the active area demonstrate lower resonant frequencies of
 (1.18 ± 0.09) GHz and (1.91 ± 0.06) GHz due to the presence of the added cat-
 300 alyst and CNT layers. Furthermore these layers cause a reduction in Q (in the
 range from 10% to 30%) compared to SMRs without the CNT layer as observed
 in Figure 4 (b) and (c). The average Q_{air} of the TSM and TLM (Figure 4 (b)
 and (c)) in all the devices with CNTs are smaller compared to SMRs without
 CNTs, due to acoustic losses added by the presence of this layer; the low density
 305 CNTs are particularly lossy because of their reduced vertical alignment as ob-
 served by SEM (Figure 3 (a)), which causes more friction-contact points. The
 effective electromechanical coupling coefficients, k_{eff}^2 , for the TSM and TLM are
 found to be $(1.7 \pm 0.2)\%$ and $(3.1 \pm 0.3)\%$ respectively. Although these values
 are significantly inferior than those reported for AlN resonators [50, 51], it is
 310 necessary to emphasize that the focus of this work has been to achieve high Q ,
 which improves the precision of determining f_r caused by low mass loads with
 sharper resonances.

In Figures 5 (a) and (b), the real part of the $Y(S)$ spectra of the SMRs
 measured in DI water with different CNT forest densities are compared with
 315 conventional SMRs without CNTs. SMRs with HD CNTs exhibit TSM and
 TLM resonances with strong amplitudes in DI water as compared with devices
 without CNTs. This is confirmed by the spectra shown in Figure 5 (a) and
 (b), which are normalized to their individual resonant frequencies for a clear
 comparison of the peak sharpness. It can be observed that the Q in water of
 320 resonators with HD CNTs is 141 and 167 for the TSM and TLM respectively.
 Although the TSM of an SMR without CNTs has a Q in water of ~ 102 as
 expected with the lower acoustic dissipation in-liquid of the shear mode, its
 TLM resonance is non-existent (Q in water ~ 3) as demonstrated by the wide
 resonance in Figure 5 (b). The MD CNTs and LD CNTs also have improved

325 Q in water for the TLM compared to devices without the CNTs as illustrated
 in Figure 5 (c). The result is significant in that the TLM has a measurable Q
 (> 100) in DI water because of the presence of the CNT layer on top. This is
 the first demonstration of the use of an interface layer such as a CNT forest for
 TLM resonance with high Q -factors in a liquid environment. In Figures 5 (c)
 330 and (d), boxplots of the Q in water of five representative devices measured are
 displayed for the TSM and TLM respectively. It is observed that the presence
 of HD CNTs on the active area isolates the resonator from the DI water leading
 to Q larger (both for the TLM and TSM) than in the cases of the SMRs without
 CNTs. For the TLM Q boxplot displayed in Figure 5 (d), the Q in DI water
 335 increases from ~ 3 to ~ 150 as the CNT forest becomes denser, confirming the
 reduced contact of the DI water with the resonator surface.

3.3. Dissipation of acoustic wave in DI water

To quantitatively evaluate the acoustic leakage into the DI water, the dissi-
 pation factor, D , which is a measure of the contribution to total energy losses
 340 to the liquid medium by the resonator, is calculated using equation 3 [52].

$$D = \frac{1}{Q_{\text{water}}} - \frac{1}{Q_{\text{air}}} \quad (3)$$

where Q_{air} is the unloaded Q in air, which includes all losses of the resonator
 and Q_{water} is the Q in a liquid environment, which additionally includes the
 losses to the liquid.

In Table 1, D is calculated for the TSM and it is observed that in the presence
 345 of MD and HD CNTs on the active area, D improves from $(0.75 \pm 0.26) \times 10^{-2}$
 to $(0.63 \pm 0.20) \times 10^{-2}$ and $(0.39 \pm 0.23) \times 10^{-2}$ respectively. Nonetheless with
 LD CNTs a higher acoustic leakage is observed as D increases to $(1.33 \pm 0.65) \times$
 10^{-2} , which can be caused by the smaller initial TSM Q_{air} of those devices.
 In Table 2 the corresponding values of D are calculated for the TLM and a
 350 remarkable reduction in acoustic leakage in DI water is observed (D decreases
 from $(31 \pm 12) \times 10^{-2}$ without CNTs to less than 2.0×10^{-2} with the presence of
 the CNTs investigated). Indeed without the CNTs, the TLM suffers from large

acoustic damping in DI water, having Q values of only ~ 3 -5, whereas with LD
 CNTs this Q value increases to ~ 64 , and with HD CNTs, an average Q value
 of ~ 160 , and $D \sim 0.45 \times 10^{-2}$ is achieved in DI water. Using taller HD CNT
 forests of length $30 \mu\text{m}$, devices operating in a TLM with a Q above 200 in water
 have been measured indicating that the TLM resonance is significantly isolated
 from the DI water droplet. This can be explained by the acoustic impedance
 mismatch provided by the high forest density CNT layer, which separates the
 resonator and the DI water. This mismatch causes the TLM to remain partially
 confined in the device, hence achieving a high Q despite the presence of a DI
 water droplet.

Table 1: Quantitative analysis of the effect of different carbon nanotube (CNT) forest densities (low density (LD), medium density (MD) and high density (HD)) on the mean shear mode quality-factor in air, Q_{air} , quality-factor in water, Q_{water} , and the dissipation factor D values. The standard deviation from the mean value is used to estimate the errors and variability in the values.

Active area	Q_{air}	Q_{water}	$D (\times 10^{-2})$
No CNT	320 ± 90	94 ± 20	0.75 ± 0.26
Low density CNT	190 ± 60	54 ± 20	1.33 ± 0.65
Medium density CNT	230 ± 60	94 ± 10	0.63 ± 0.20
High density CNT	210 ± 40	110 ± 60	0.39 ± 0.23

Table 2: Quantitative analysis of the effect of different carbon nanotube (CNT) forest densities (low density (LD), medium density (MD) and high density (HD)) on the mean longitudinal mode quality-factor in air, Q_{air} , quality-factor in water, Q_{water} , and the dissipation factor D values. The standard deviation from the mean value is used to estimate the errors and variability in the values.

Active area	Q_{air}	Q_{water}	$D (\times 10^{-2})$
No CNT	790 ± 180	3 ± 1	30.9 ± 11.7
Low density CNT	220 ± 120	64 ± 40	1.09 ± 0.93
Medium density CNT	340 ± 110	68 ± 30	1.19 ± 0.63
High density CNT	590 ± 120	160 ± 60	0.45 ± 0.26

3.4. Sensitivity to mass binding with BSA in DI water

The effect of exposing BSA solutions of concentrations ranging from 0.05
365 $\text{mg}\cdot\text{mL}^{-1}$ to $2.5 \text{ mg}\cdot\text{mL}^{-1}$ on both the TSM and TLM resonances with devices
having $\sim 15 \mu\text{m}$ tall CNT layers are shown in Figure 6. A smaller (approx-
imately by a factor of 7) relative frequency shift ($\Delta f_r/f_r \sim -39.9 \text{ ppm}$) is
demonstrated by the TSM compared to the TLM ($\Delta f_r/f_r \sim -337 \text{ ppm}$) for
the highest BSA concentration ($2.5 \text{ mg}\cdot\text{mL}^{-1}$), suggesting the potential for im-
370 proved performance in-liquid using a TLM resonance. At BSA concentrations
higher than $1 \text{ mg}\cdot\text{mL}^{-1}$, the relative frequency shift saturates as shown in Fig-
ure 6 because the majority of the exposed binding areas on the CNT forest are
occupied by BSA and no further BSA molecules can attach.

A comparison of mass binding over a time span of 8 mins for HD CNT forests
375 of height $\sim 15 \mu\text{m}$ and $\sim 30 \mu\text{m}$ is shown in Figure 7 (a). Although achieving
 Q -factors exceeding 200 in water (inset of Figure 7 (a)), the Δf_r observed are
negligible ($< -10 \text{ ppm}$) for the $30 \mu\text{m}$ tall CNT forest in spite of using high
BSA concentrations ($2.5 \text{ mg}\cdot\text{mL}^{-1}$). Indeed 8 mins after dropping the BSA on
the SMR, the $\Delta f_r/f_r$ of the TLM is approximately -340 ppm with a CNT forest
380 of $15 \mu\text{m}$ in height compared to $\Delta f_r/f_r$ of $+6.6 \text{ ppm}$ for the $30 \mu\text{m}$ tall CNT
forest. This positive shift can be attributed to noise in the measurement or a
temperature drift caused by the cooling of the resonator as the liquid evaporates.
Similarly smaller changes in f_r (-6.2 ppm compared to -39.9 ppm) with the
TSM modes are recorded as the CNT forest height increased from $15 \mu\text{m}$ to 30
385 μm . The noise in the measurement is influenced mostly by the device intrinsic
response whereas the binding speed of the BSA to the CNTs affects the response
time. These results suggest that the mechanical vibration to sense mass loading
is dependent on the height of the CNT forest. When the CNT forest is very
tall (for example $30 \mu\text{m}$), the binding of BSA molecules on the forest does not
390 cause significant variation in the frequency response.

For biosensor applications, the TLM resonance should be able to propagate
to some extent to the region where biomolecules attach –the upper part of the
CNT forest is the binding region for these SMRs as shown schematically in

Figure 7 (b). Evidently the CNT forest height needs to be tuned to have only
395 a partial isolation from the DI water while acting as a probe for biomolecule
binding. Accordingly the design of the CNT forest thickness requires a com-
promise between acoustic isolation from the liquid and sensor mass sensitivity.
The precision of this thickness tuning is however, not as critical as in the case of
microchannels. Nevertheless it is necessary to identify the caveats in fabricat-
400 ing CNT forests to isolate the TLM resonance in liquid for biological detection.
First the forest can be so tall that there is no interaction of the acoustic wave
with the liquid-CNT interface as illustrated in Figure 7 (b), and second is the
fact that the CNT forests easily bundle when used in liquids that have low
surface tension such as isopropyl alcohol (IPA) and acetone. This type of den-
405 sification consequently leads to voids or can expose the resonator surface to the
liquid, causing a significant energy dissipation. In Figure 8, the impact on the
active area after immersing in different liquids and drying is shown. DI water
causes no major structural damage and the CNT forest maintains its integrity
as illustrated in Figure 8 (b). In this work the CNT coated SMRs have been in
410 fact observed to retain their high Q -factor in DI water even after a few in-liquid
measurement and dry cycles. This is a highly desirable property for applica-
tions in biosensing as the SMRs with CNTs are robust and can be re-used. In
contrast there is significant exposure of a dried active area to liquids after IPA
immersion shown in Figure 8 (c) and (d).

415 CNT coated SMRs that have been exposed to IPA have over 80% decrease
in TLM Q -factor when used afterwards in DI water, which is close to typical
TLM SMRs without CNTs, therefore confirming the higher acoustic energy
dissipation into the liquid through the exposed regions. A further shortcoming
of growing CNTs on gravimetric sensors is the high temperature of CVD, which
420 renders them unsuitable for plastic substrates. As an alternative, CNTs could be
grown by CVD on an independent substrate and prepared into a liquid solution
using an ultrasonic spinner. CNT layers on gravimetric sensors can then be
deposited either by drop-casting or spin-coating, thereby eliminating the need
for high temperature processing. In this case however, dense and VA-CNTs

425 would not be feasible and other methods such as indium-assisted transfer of
VA-CNTs reported by Barako *et al.* [53] would be necessary.

4. Conclusions

In this work, the growth of CNTs of different morphologies on the active area
of SMRs is achieved by CVD at 600 °C by varying the catalyst (Fe) thickness.
430 The purpose of the CNT layer is to isolate the resonator active areas from
liquids such as DI water to reduce acoustic damping by confining the acoustic
wave in the SMR. AlN SMRs with both a TSM (1.1 GHz) and a TLM (1.9 GHz)
resonance are fabricated to assess and compare the performance of CNT-coated
devices to SMRs without CNTs in DI water. It is demonstrated that SMRs with
435 highly packed CNT forests achieve the lowest TLM dissipation factors, D , of
(0.45 ± 0.26) $\times 10^{-2}$ compared to (31 ± 12) $\times 10^{-2}$ in uncoated SMRs. Additionally
TSM resonances also benefit from the CNT layer and have a lower acoustic wave
leakage (a decrease in D from (0.75 ± 0.26) $\times 10^{-2}$ to (0.39 ± 0.23) $\times 10^{-2}$ is
observed) into the DI water droplet due to the presence of a highly packed CNT
440 forest on the active area. Despite the presence of a tall CNT forest of up to ~ 15
 μm height, the SMRs are sensitive to mass loading caused by BSA solutions.
The result in this work is significant in that the TLM can be made to operate in
DI water with the presence of a CNT isolation layer, which can potentially lead
to the successful scaling up and commercialization of FBAR based biosensors.

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Figure legends

Figure 1: Structure of solidly mounted resonators (SMRs) fabricated with carbon nanotubes (CNTs). (a) Schematic of the SMR structure fabricated on Si showing the 5 layer acoustic reflector, the piezoelectric AlN layer and the top electrode on which vertically aligned (VA) CNTs are grown to cover the active area. (b) A magnified view of the active area fully isolated by the presence of a forest of CNT. (c) SEM cross-section of an inclined *c*-axis AlN SMR demonstrating the presence of the 5 layer reflector, an Ir bottom electrode of ~ 130 nm and an AlN piezoelectric film ~ 1.2 μm thick inclined at $\sim 24^\circ$ to the surface normal.

Figure 2: Growth schematic with substrate heated until 600 °C at 200 °C/min in NH₃ (Stage 1) and stabilized to form nanoparticles (NPs) (Stage 2) C₂H₂ is added to grow carbon nanotubes (CNTs) and both NH₃ and C₂H₂ are switched off (Stage 3) before cooling in Ar.

Figure 3: Characterization of carbon nanotubes (CNTs) (a) (i) Electron micrographs of CNTs grown on devices with the 0.5 nm Fe giving tall and high density forests. (ii) Cross-sections illustrating the heights of the CNTs and their alignment, 4.5 nm Fe gives randomly aligned CNTs. (iii) Optical images of the devices showing a significant contrast of the CNTs grown with 0.5 nm Fe and 4.5 nm Fe as the height and density decrease. (b) Raman spectra of the CNT morphologies grown and G and D -peaks normalized intensity ratio (I_G/I_D), which decreases as Fe increases.

Figure 4: Electrical characterization of devices in air with and without CNTs. (a) shows the $Y(S)$ spectra of typical devices with (blue solid line) and without high density (HD) CNTs (red dashed line) on the active area, exhibiting a TSM at f_r of 1.12 GHz, a spurious mode at 1.6 GHz and a TLM at 1.89 GHz. Graphs have been displaced for clarity. (b) Box and whisker diagram of the Q in air for both the TSM at ~ 1.1 GHz and the TLM at ~ 1.9 GHz of 5 representative devices measured in each type of CNT (low density (LD), medium density (MD) and HD) showing a decrease in Q_{air} due to parasitics added by CNTs. The red middle line is the median, whereas the upper and lower bounds of the box are the first and third quartiles respectively; the terminals are outliers.

Figure 5: Electrical characterization of devices in DI water. (a) Real part of the $Y(S)$ for the TSM in water for devices without CNTs, with low density CNTs (LD CNTs), medium density CNTs (MD CNTs) and high density CNTs (HD CNTs), (b) Real part of TLM $Y(S)$ in water showing resonance (Q_{water} as high as 167) for all the CNT types investigated compared to SMRs without any CNTs. (c) Box and whisker diagram for the quality-factor in DI water, Q_{water} , for both the TSM and the TLM resonances of 5 representative devices measured in each type of SMRs illustrating the increase in Q_{water} by the isolation caused by the CNT layer. The red middle line is the median, whereas the upper and lower bounds of the box are the first and third quartiles respectively; the terminals are outliers.

Figure 6: Relative resonant frequency shifts ($\Delta f_r/f_r$) for the shear and longitudinal modes with different bovine serum albumin (BSA) concentrations in mg/mL. Dashed lines are guides for the eye. The longitudinal mode (blue line) with resonance frequency, $f_{1,r} = 1.91$ GHz, has a larger shift compared to the shear mode (dark line) with resonant frequency $f_{s,r} = 1.12$ GHz. A saturation point is reached at high concentrations. Inset shows a schematic of the droplet of BSA solution on top of the 15 μm tall carbon nanotube (CNT) forest. The devices used in this test had quality-factors of ~ 150 in DI water.

Figure 7: Mass sensitivity with different carbon nanotube (CNT) heights (a) Comparison of the relative frequency shifts with a BSA concentration of $2.5 \text{ mg}\cdot\text{mL}^{-1}$ for the TSM and TLM with time for SMRs with CNTs of $\sim 15 \text{ }\mu\text{m}$ and $\sim 30 \text{ }\mu\text{m}$ in height. Lines are guides for the eye. The TLM with $15 \text{ }\mu\text{m}$ tall CNT has the highest Δf_r of -337 ppm . Inset shows a comparison of the Q in DI water for the TLM with different VA-CNT forest heights. (b) Schematic representation of the dissipation of the TLM with CNT forests of different heights, illustrating the larger amplitude resonance confined in the resonator with taller CNTs but no vibration on the surface. With shorter CNTs, acoustic wave dissipation occurs in liquid but the resonance is still significant for mass detection whereas without CNTs, all the energy is radiated in the liquid.

Figure 8: SEM images of the active area of the SMR with the HD CNTs grown, in (a) the CNT immediately after growth, (b) Dried after DI water droplet has been added, (c) Dried after IPA has been added showing exposed resonator surface (d) Voids left after IPA densification in some devices that allow liquids to penetrate the forest to the resonator.