To my parents
Acknowledgements

First I would like to thank my advisor Prof. Matteo Rinaldi for providing me such precious opportunity to work in the field of MEMS/NEMS design and his great support during my research. Especially, it is a big honor to be among Prof. Rinaldi’s first generation of graduate students. It is in our Northeastern Sensors & Nano Systems Lab (NS&NS Lab) that I learned how to do research, fabricate NEMS resonators, write papers, give presentations, and so on.

I also want to thank my colleague, Yu Hui, who shared many helpful experiences and knowledge with me and our collaborators from Physics Department, Prof. Swastik Kar and Fangze Liu, who provided not only graphene samples but also very valuable technical and professional advices.

I am very grateful to the staff of the George J. Kostas Nanoscale Technology and Manufacturing Research Center at Northeastern University, where the devices reported in this thesis were fabricated.

Most of all, I would like to express immense gratitude to my parents, who always supported me mentally and financially, and helped me to overcome many of the professional and personal issues that I encountered.
Abstract

The physical and electrical properties of the metal electrodes fundamentally limit volume and frequency scaling of conventional Micro and Nano Electro Mechanical Systems (MEMS/NEMS) piezoelectric resonators. Furthermore, it has been shown that metal electrode damping and interface strain are responsible for the $Q$ limits in conventional AlN Lamb wave resonators. In this thesis a stepping stone towards the development of metal-free piezoelectric NEMS resonators for ultra-high resolution and fast resonant sensing is set by integrating a 2D graphene electrode on top of an AlN resonant nano-plate in lieu of a relatively thicker and heavier metal electrode. Despite a bottom metal interdigital electrode is still employed in this first prototype, the fabricated Graphene-Aluminum Nitride Nano Plate Resonator (G-AlN NPR) is characterized by reduced mass (~43%) and volume (~16%), increased sound velocity, hence resonant frequency (~23%), and improved device figure of merit ($k_t^2 Q \approx 18$) compared to a conventional AlN NPR device.

The achieved high electromechanical performance of the ultra-thin, low mass and high frequency G-AlN nanomechanical resonator enabled the implementation of a low phase noise (-87 dBC/Hz @ 1kHz offset and -125 dBC/Hz floor) single transistor oscillator. The experimental results also demonstrate the great potential of the proposed technology for the implementation of a new class of ultra-sensitive and low noise G-AlN resonant sensors.
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1. INTRODUCTION

In recent years, Micro and Nano Electro Mechanical Systems (MEMS/NEMS) resonators have been widely used for multiple sensing applications thanks to the unique combination of extremely high sensitivity to external perturbations and ultra-low noise performance. Among different MEMS/NEMS resonant sensors, the AlN nano plate resonant sensor (NPR-S) technology [1], which involves exciting high frequency (100 MHz to 10 GHz) bulk acoustic waves in piezoelectric nano plates (thickness < 1 µm) made out of AlN, has emerged as one of the most promising solutions for the realization of extremely sensitive, miniaturized and low power chemical sensors [2], thermal detectors [3], and magnetic field sensors [4]. The reduced mass and high frequency of operation of the nanomechanical resonant elements combined with their high \( Q \) factor values and power handling capabilities make the AlN NPR-S capable to achieve unprecedented values of limit of detection and detection speed [2-5].

The performance of AlN NPR-S in terms of sensitivity, limit of detection and detection speed can be further improved by scaling thickness and decreasing the equivalent density of the Aluminum Nitride Nano Plate Resonator (AlN NPR) maintaining, at the same time, high values of \( Q \) factor and transduction efficiency [5]. Such performing device scaling is currently fundamentally limited by the physical and electrical properties of the metal electrode employed to provide the excitation electrical signal to the piezoelectric nano resonator. Ultra-thin metal electrodes would
introduce extremely high values of electrical resistance which would electrically load the $Q$ factor of the resonant element limiting the resolution of the sensor. Thicker metal electrodes which are not scaled proportionally to the AlN plate would instead mechanically load the device negatively affecting both its $Q$ factor and transduction efficiency. Furthermore, it has been recently shown that metal electrode damping and interface strain are responsible for the $Q$ limits in conventional AlN Lamb wave resonators [6].

The work presented in this thesis introduces an ultra-thin and light 2D electrode material, graphene, into current Aluminum Nitride Nano Plate resonator technology. A stepping stone towards the development of ultra-high resolution and fast resonant sensors is set by integrating a 2D graphene electrode on top of an AlN resonant nano plate [7] and using such G-AlN resonator to implement a low phase noise single transistor oscillator [8]. Graphene is a one-atom thick layer of the mineral graphite with excellent electrical conductivity and extremely light weight. The ultra-low mass 2D graphene layer is employed, in lieu of a relatively thicker and heavier metal film, as top electrically floating electrode in the lateral field scheme [5] used to excite vibration in the piezoelectric nano plate. Such 2D graphene top layer not only represents the thinnest and lightest conductive electrode ever used to excite vibration in a piezoelectric NEMS resonator but it also has the potential to be used as an effective chemical interactive material with the largest possible surface to volume ratio [9].

The thesis is organized in the following chapters:
In Chapter 2, after reviewing the mechanism and fundamental parameters of the Aluminum Nitride Nano Plate Resonator (AlN NPR), the analysis and optimization of the detection capabilities of Aluminum Nitride Nano Plate Resonant Sensor (AlN NPR-S) are introduced. The design and fabrication solutions of the proposed Graphene-Aluminum Nitride Nano Plate Resonators (G-AlN NPR) as well as simulation verification using Finite Element Method (FEM) are presented. Then, the experimental demonstration of the first of G-AlN NPR prototypes is presented. These novel devices achieve high electromechanical performance, comparable to conventional AlN NPRs despite the substantially reduced mass and volume of the resonant structure, which translates in improved sensitivity and limit of detection. Measured Temperature Coefficient of Frequency (TCF) of the G-AlN NPR are reported and discussed at the end of Chapter 2.

In Chapter 3, the design and implementation of a single transistor oscillator based on a G-AlN NPR are discussed. The noise performance of such sensor prototype and its relationship with the resonant device quality factor are presented and analyzed.

In Chapters 4, the main achievements of this research work are summarized and discussed and the vision for a new class of ultra-sensitive gravimetric sensors based on metal-free G-AlN NPR is presented as future work.
In recent years, the demand for highly miniaturized sensors capable of detecting extremely small concentrations of multiple gaseous analytes has grown. The necessity to detect such small concentrations requires reliably measuring extremely small variations in the sensor output signal. In this perspective, optimal sensor performance is attained by synthesizing a transducer that occupies a large area (which facilitates efficient transduction) and is very thin (which allows fabricating low mass devices with ultra-high sensitivity). Suspended membranes with thickness in the nanometer range are therefore desirable. Aluminum Nitride Nano Plate Resonator (AlN NPR) firstly proposed by Prof. Matteo Rinaldi is a particularly representative example of high performance bulk mode acoustic NEMS resonant sensors which involve exciting high frequencies bulk acoustic waves in a piezoelectric nano-plate (thickness 50 ~ 500 nm) made of Aluminum Nitride (AlN). Such AlN Piezoelectric Nano-Plate Resonant Sensor (NPR-S) technology is not only characterized by high values of sensitivity, due to the reduced mass and high frequency of operation of the nanomechanical resonant element, but it is also associated with low noise performance, due to the combination of high quality factor, $Q$, and power handling capability of the bulk acoustic wave NEMS resonators [10].
In addition, the AlN nano-plate composing the NPR-S can be efficiently actuated and sensed piezoelectrically on-chip solving the fundamental transduction issues associated with electrostatically transduced NEMS resonators and enabling the use of compact and low power CMOS circuits for electronic readout.

The performance of AlN NPR-S in terms of sensitivity, limit of detection and detection speed can be further improved by scaling thickness and decreasing the equivalent density of the AlN NPR maintaining, at the same time, high values of Q factor and transduction efficiency. The physical and electrical properties of the metal electrodes fundamentally limit volume and frequency scaling of conventional MEMS/NEMS piezoelectric resonators. In this thesis the replacement of conventional metal electrodes with graphene electrodes is proposed to solve the fundamental scaling issue associated to metal loading in piezoelectric NEMS resonators. Such 2D graphene top layer not only represents the thinnest and lightest conductive electrode ever used to excite vibration in a piezoelectric NEMS resonator but it also has the potential to be used as an effective chemical interactive material with the largest possible surface to volume ratio.

In this chapter, the mechanism and fundamental parameters of AlN NPR is firstly reviewed. After that, the analysis and optimization of the AlN NPR-S detection capabilities are introduced. The design and fabrication solutions of proposed Graphene-Aluminum Nitride Nano Plate Resonators (G-AlN NPR) as well as simulation verification using FEM are presented. Then, the first prototypes of G-AlN NPRs are presented.
2.1 Aluminum Nitride Nano Plate Resonators

Aluminum Nitride is a dielectric material that belongs to the dihexagonal polar class of crystals and exhibits direct piezoelectric effect (the internal generation of electrical charge resulting from an applied mechanical force). As an effective way of describing this piezoelectric phenomenon into equations, the electromechanical coupling can be expressed in the d-form piezoelectric coefficient matrix (1):

\[ S = sT + d^T E \]
\[ D = dT + \varepsilon E \]

Where \( S \) is the strain (6×1 matrix), \( T \) is the stress (6×1 matrix), \( E \) is the electric field (3×1 matrix), \( D \) is the electric displacement (3×1 matrix), \( s \) is the compliance (6×6 matrix), \( \varepsilon \) is the permittivity (3×3 matrix) and \( dT \) is the transpose of the strain-charge form (d-form) piezoelectric coefficient (3×6 matrix). For AlN, the \( d \) matrix is given by Eq. (2)

\[
\begin{bmatrix}
0 & 0 & 0 & 0 & -4 & 0 \\
0 & 0 & 0 & -4 & 0 & 0 \\
-1.98 & -1.98 & 4.98 & 0 & 0 & 0
\end{bmatrix}
\]

The \( d_{33} \) coefficient has been exploited in film bulk acoustic wave resonators (FBARs) for duplexer applications [11-12], but the resonant frequency is set by the thin film thickness, which is not suitable for single chip multi-frequency operation. Instead, by using the \( d_{31} \) piezoelectric coefficient and applying an AC electric field in
the thickness direction, in-plane displacement or lateral vibration can be excited in the MEMS structure (Figure 2.1). Such lateral-extensional mode of vibration is employed for the piezoelectric AlN NPRs presented in this work.

![Figure 2.1 Schematic representation of the dihexagonal structure of AlN. The fundamental X(1), Y(2) and Z(3) directions are indicated. As shown, the anisotropic nature of the film permits the excitation of contour mode shapes through the d31 piezoelectric coefficient](image)

A conventional AlN NPR is composed of an AlN film sandwiched between two metal electrodes (Figure 2.2). When an AC voltage is applied to the interdigital electrode a contour-extensional mode of vibration is excited through the equivalent $d_{31}$ piezoelectric coefficient of AlN [10].
Figure 2.2 Schematic representation of a conventional AlN Nano Plate Resonator. The inset shows a FEM simulation of the device mode of vibration

Given the equivalent mass density, $\rho_{eq}$, and Young’s modulus, $E_{eq}$, of the material stack (AlN and electrodes) that forms the resonator, the center frequency, $f_0$, of this laterally vibrating mechanical structure, is univocally set by the pitch, $W_0$, of the metal electrode patterned on the AlN nano plate. The resonance frequency of the device can be expressed as Eq. (3) [13]

$$f_0 = \frac{1}{2W_0} \sqrt{\frac{E_{eq}}{\rho_{eq}}}$$  \hspace{1cm} (3)

Several of these unitary cells of width, $W_0$ (known as fingers), are arrayed together and excited in an alternating fashion (two adjacent fingers are excited 180° out of phase with respect to each other) so as to form an equivalent symmetric lamb wave [14-16] in the AlN nano plate (Figure 2.3).
The other two geometrical dimensions, thickness, $T$, and length, $L$, set the equivalent electrical impedance of the resonator and can be designed independently of the desired resonance frequency. The number of fingers, $n$, their length, $L$, (also known as aperture of the transducer) and the film thickness, $T$, are used to set the equivalent resonator electrical capacitance, $C_0$, and its motional resistance, $R_m$, [10] as expressed in Eq. (4)

$$R_m \propto \frac{T}{nL}$$

$$C_0 \propto \frac{nLW_0}{T}$$

(4)

These parameters and equations will be used to guide the design of G-AlN NPR in the following sections.
2.2 Graphene Enabled Ultimate Scaling of AlN NPR

A fundamental parameter for gravimetric sensing applications is the resonator sensitivity, $S$, to mass per unit area, which, for a AlN NPR-S loaded on its top surface, can be expressed as in Eq. (5) [2, 17]

$$S = -\frac{f_0}{2\rho_{eq}T}$$  \hspace{1cm} (5)

It is worth noting that the resonance frequency, $f_0$, and the thickness, $T$, of the AlN NPR-S are two independent variables while for FBARs they are intrinsically coupled and cannot be set independently from one another. This is an important and unique advantage of AlN NPR-S. In fact, it permits to set the frequency of operation of these devices according to the specifications of the desired application and independently obtain the required value of mass sensitivity by scaling the device thickness.

Nevertheless, the mass sensitivity of the device cannot be considered the only important parameter for the design of a high performance gravimetric sensor. In fact, the limit of detection, LOD, of the sensor (smallest amount of adsorbed mass per unit area that can be resolved) is defined as in Eq. (6) [18, 19]

$$LOD = \frac{\Delta f_{\text{min}}}{S}$$  \hspace{1cm} (6)
Where $\Delta f_{\text{min}}$ indicates the minimum frequency shift detectable by the sensor readout which is fundamentally limited by noise induced frequency fluctuations. Although multiple sources of noise affect the frequency stability of the device, only thermomechanical noise is considered in this analysis as the ultimate limiting factor to guide the device design, Eq. (7)

$$\Delta f_{\text{min}} \propto \sqrt{\frac{k_B T_0 B}{P \frac{f_0}{Q}}}$$

(7)

Where $k_B$ is Boltzmann constant, $T_0$ is temperature, $B$ is the measurement bandwidth and $P$ is the driving power. By combining the two Eq. (5) and Eq. (7) into LOD expression Eq. (6), we get Eq. (8)

$$LOD \propto \frac{\rho_{eq} T}{Q}$$

(8)

Thus, it can be concluded that the requirements for achieving best resonant transducer are, ultra-low mass, ultra-thin resonant plate and the last but not least high quality factor.

Such performing device scaling is currently fundamentally limited by the physical and electrical properties of the metal electrode employed to provide the excitation electrical signal to the piezoelectric nano resonator. Ultra-thin metal electrodes (scaled proportionally to the AlN plate) would introduce extremely high values of electrical resistance which would electrically load the $Q$ factor of the
resonant element limiting the resolution of the sensor. Thicker metal electrodes (not scaled proportionally to the AlN plate) would instead mechanically load the device (heavy mass on top of the nanoscale piezoelectric resonant plate) negatively affecting both its $Q$ factor and transduction efficiency.

The capability to excite a high frequency ($\sim 700 \text{ MHz}$) and high $Q$ ($\sim 700$) lateral-extensional mode of vibration in AlN nano-plates as thin as 50 nm has been recently demonstrated [20]. However, relatively thick ($\sim 25 \text{ nm}$) platinum and gold metal films were employed as electrode materials for such 50 nm thick AlN nano plate resonators in order to maintain a low value of the electrode electrical resistance. Such relatively thick and heavy metal electrodes, compared to the ultra-thin and light AlN nano-plate, prevent volume and mass scaling of the device. More than 80% of the total mass of such 50 nm thick AlN NPR is associated with the metal electrodes, which drastically limits both the sensitivity and the noise performance of the device (mechanical loading effect of the electrode reduces $Q$).

In this thesis, 2D graphene electrodes are proposed to solve this fundamental scaling issue. Graphene is a single-atomic-layer, 2D system composed solely of carbon atoms arranged in a hexagonal honeycomb lattice. This atomically thick sheet of carbon is an excellent electrical conductor, with exceptionally high mobility for both electrons and holes ($\sim 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [21, 22]. The ultra-low mass 2D graphene layer is employed, in lieu of a relatively thicker and heavier metal film, as top and bottom electrode in the lateral field scheme used to excite contour-extensional vibration in the piezoelectric nano plate (Figure 2.4). The ultra-thin (0.6 nm) and light
graphene electrodes will enable the ultimate scaling down to just 10nm of AlN nano plate [23].

Figure 2.4 Schematic representation of a G-AlN NPR excited to vibrate at high frequency in its contour-extensional mode

Such 2D graphene top layer not only represents the thinnest and lightest conductive electrode ever used to excite vibration in a piezoelectric NEMS resonator but it also has the potential to be used as an effective chemical interactive material with the largest possible surface to volume ratio [9]. Furthermore, it has been recently shown that the metal electrode damping and interface strain are dominant in the $Q$ degradation of high frequency contour mode vibration [6]. However, atomic monolayer graphene introduces lowest electrode damping and interface strain than any metal electrodes, hence the metal-free G-AlN NPR automatically yields high $Q$ performance. According to given Eq. (8) above, the Limit of Detection of a
gravimetric sensor based on this new class ultra-thin resonator can be pushed down to sub-zeptogram per micro square.

Table 2.1 shows a comparison between G-AlN NPR-S and four other resonant sensor technologies in terms of limit of detection, multiple sensitivities, interface to 50 Ω electronics and small form factor. Thanks to the very reduced volume of G-AlN NPRs, hence very small footprint, this technology has great advantages in terms of miniaturization and IC integration capabilities comparing to Quartz Crystal Microbalances (QCMs) [24] and Surface Acoustic Wave (SAW) devices [25]. For Film Bulk Acoustic Resonators (FBARs) [11, 12] and QCM, the operating frequency is set by the thickness of the piezoelectric material, which excludes the capability of these devices to provide for multiple frequencies of operation (hence mass sensitivities) on the same substrate and their employment for the fabrication of multi frequency single chip sensor arrays capable of selectively detecting multiple analytes over a wide range of concentrations. As for NEMS beam resonators [26], they require the use of cumbersome, complex and power inefficient read-out techniques due to the incompatible interface to common value for source and load impedances (50 Ω) of radio-frequency (RF) systems.
Table 2.1 comparison between G-AlN NPR-S and four other resonant sensor technologies

<table>
<thead>
<tr>
<th></th>
<th>QCM</th>
<th>SAW</th>
<th>FBAR</th>
<th>NEMS Beam</th>
<th>G-NPRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of detection</td>
<td>ag/μm²</td>
<td>ag/μm²</td>
<td>ag/μm²</td>
<td>zg/μm²</td>
<td>Sub-zg/μm²</td>
</tr>
<tr>
<td>Multiple sensitivities</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
</tr>
<tr>
<td>Interface to 50Ω electronics</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
</tr>
<tr>
<td>Small form factor</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
</tr>
</tbody>
</table>
2.3 1\textsuperscript{st} Generation G-AlN NPR

As proof of concept of the proposed G-AlN NPR with enhanced detection capabilities according to what is described in section 2.2, a first prototype of G-AlN NPR was designed and fabricated.

The three-dimensional schematic representation of such first prototype of G-AlN NPR is shown in Figure 2.5.

\textbf{Figure 2.5} 3D schematic representation of the first prototype of G-AlN NPR

In this first prototype, a lateral field excitation with floating top electrode (LFE-F) is employed to excite a higher order contour-extensional mode of vibration in the AlN nano-structures. The LFE-F involves depositing the 500 nm AlN film (forming the resonant nano plate) on top of an interdigital bottom electrode (50 nm) employed to excite the higher order lateral-extensional mode of vibration. The
electrically floating top electrode is instead used to confine the excitation electric field across the thickness of the piezoelectric layer. It is worth noting that without the electrically conductive top electrode the excitation electric field would not be effectively confined across the thickness, $T$, of the device, hence the electromechanical coupling coefficient, $k_t^2$, of the nanomechanical structure would be approaching $\sim 0$ [27] (Figure 2.6) and it would not be possible to excite the high frequency contour-extensional mode of vibration in such ultra-thin (500 nm) AlN nano plate. In this work, graphene is employed for the first time as an ultra-thin and light top electrically floating electrode.

![Figure 2.6 schematic representation of electric field in AlN Nano Plate](image)

The effective device area of this first prototype of G-AlN NPR was designed to be $60 \, \mu m \times 200 \, \mu m$, the pitch, $W_0$, of bottom Platinum (Pt) finger electrode was set to be 20 $\mu m$ and the thickness of AlN nano plate and bottom Pt electrode are
500 nm and 50 nm respectively, resulting in a high order contour-extensional mode resonator working at high resonance frequency of approximately 230 MHz.

For future comparison, a conventional AlN NPR based on the same core design but employing a 100 nm thick gold top electrode instead of the 2D graphene top electrode was designed for reference (gold is typically used as top metal electrode in NEMS resonant sensors since it can be easily functionalized with thiolated ligands [2]).

A 2D finite element method (FEM) simulation was performed using COMSOL Multiphysics to investigate vibration mode, operation frequency and expected sensitivity for both the first prototype of G-AlN NPR and the reference device. Given to the designed dimensions, the resonant frequencies were found at 230 MHz and 185 MHz for G-AlN NPR and the reference device respectively (Figure 2.7). And the vibration mode of G-AlN NPR was confirmed as contour-extensional mode (Figure 2.8).
Figure 2.7 Admittance plots from 2D finite element method (FEM) simulation of the first prototype of G-AlN NPR (a) and the conventional AlN NPR (b)
Figure 2.8 Vibration mode from 2D finite element method (FEM) simulation of G-AlN NPR shows in-plane compress and extension

Table 2.2 compares the calculated sensitivity, $S$ (kHz·μm$^2$/fg) of the G-AlN NPR with the reference device. More than 2 fold improvement in sensitivity is achieved with this first prototype of G-AlN NPR-S.

<table>
<thead>
<tr>
<th></th>
<th>$f_0$(MHz)</th>
<th>$\rho_{eq}$(kg·m$^{-3}$)</th>
<th>$E_{eq}$(GPa)</th>
<th>$T$(μm)</th>
<th>$S$(kHz·μm$^2$/fg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>185</td>
<td>6220</td>
<td>350</td>
<td>0.65</td>
<td>22.8</td>
</tr>
<tr>
<td>G-AlN</td>
<td>230</td>
<td>4192</td>
<td>396</td>
<td>0.55</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Table 2.2 Comparison between the sensitivities, $S$ of the G-AlN NPR and the reference. $\rho_{eq}$, $E_{eq}$ and $T$ are the equivalent mass density, Young’s modulus and thickness of the material stack respectively.
A combination of top-down microfabrication techniques (6 masks) and bottom-up growth for graphene was employed to fabricate the G-AlN NPR of this work (Figure 2.7). A high resistivity (>10^4 Ω·cm) Silicon (Si) wafer was used as substrate. A 50 nm thick Platinum (Pt) film was sputter-deposited and patterned by lift-off on top of the Si substrate to define the bottom interdigital electrode. Then, the 500 nm AlN film (stress 60 MPa and FWHM 2.2°) was sputter-deposited and then etched by Inductively Coupled Plasma (ICP) etching in Cl₂ based chemistry to define the shape of the resonant nano plate. Vias to access the bottom electrode were etched by H₃PO₄. Then, a 100 nm thick gold (Au) film was sputter-deposited and patterned by lift-off to form the probing pads.
**Figure 2.7** Microfabrication process: (a) sputter deposition and lift-off of Pt bottom electrode; (b) sputter deposition of AlN, wet etch to open vias and dry etch to define device lateral dimensions; (c) sputter deposition and lift-off of top Au probing pads; (d) graphene transfer and patterning; (e) graphene protection and XeF₂ dry release of the G-AlN NPR. Steps (a) to (c) were processed at wafer level, while (d) and (e) at the die level.

A macroscopic sheet of graphene (1.5x1.5 cm limited by furnace dimensions) was grown directly on a copper (Cu) foil using a chemical vapor deposition (CVD) method [28] and then the graphene sheet was coated with a thin layer of poly-methyl methacrylate (PMMA) and released by etching the Cu substrate with aqueous iron (III) chloride (FeCl₃) solution. The graphene/PMMA sheet was then rinsed in deionized (DI) water and placed on top of the previously processed AlN NEMS die. The transfer of the graphene layer on the AlN NEMS die was completed by dissolving the PMMA in acetone. (Figure 2.8)

**Figure 2.8** Graphene transfer process
The graphene layer transferred on top of the AlN NEMS die was then patterned using standard lithography (Photoresist S1818 was used as mask layer) and oxygen plasma etching. In order to avoid unintentional doping of the graphene layer during the final NEMS resonator release step in XeF$_2$ [29] photoresist S1818 was again deposited by spin coating on top of the graphene-NEMS die and patterned with AlN dry etch mask using standard lithography to protect the graphene electrodes. Finally, the G-AlN NEMS structure was released from the substrate by XeF$_2$ isotropic etching of Silicon and, after that, the photoresist S1818 was removed using a conventional photoresist solvent 1165.

The fabricated first prototype of G-AlN NPR is shown in optical microscope SEM images below (Figure 2.8 and 2.9). Both of them show that a certain unremovable thin film was left after release process. And the peeled off parts introduced many defects to the graphene layer.

Figure 2.8 Optical microscope image of three G-AlN NPRs. The thin film was formed during XeF$_2$ etching and could not be chemically removed by conventional photoresist solvent or acetone
Figure 2.9 SEM image of a G-AlN NPR. The graphene was damaged by the thin film left from the last step of fabrication process.

The fabricated G-AlN NPR was tested at room temperature and atmospheric pressure in a RF probe station and its electrical response was measured by an Agilent E5071C network analyzer after performing a short–open–load calibration on a reference substrate. The electromechanical performance of the device was extracted by Butterworth-Van Dyke (BVD) model fitting (Figure 2.10) and compared to the reference device (Figure 2.11).
Figure 2.10 Measured admittance and BVD fitting of the fabricated G-AlN NPR

Figure 2.11 Measured admittance and BVD fitting of the conventional AlN NPR
Table 2.3 shows the comparison between the BVD model fitting parameters of the fabricated G-AlN NPR and the conventional AlN NPR. Higher operating frequency and was achieved with the G-AlN NPR due to its very reduced mass. However, graphene electrode introduced a relatively high value of electrical resistance, $R_s$, which electrically loaded the resonant system and largely degraded $k_t^2Q$. Besides, the thin film left after release process damped the vibrating nano plate which further aggravates the performance of the G-AlN NPR.

<table>
<thead>
<tr>
<th></th>
<th>$f_0$</th>
<th>$Q_m$</th>
<th>$k_t^2$</th>
<th>$C_0$</th>
<th>$R_m$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>200MHz</td>
<td>1015</td>
<td>1.81%</td>
<td>281fF</td>
<td>189Ω</td>
<td>98Ω</td>
</tr>
<tr>
<td>G-AlN</td>
<td>245MHz</td>
<td>596</td>
<td>1.78%</td>
<td>237fF</td>
<td>320Ω</td>
<td>460Ω</td>
</tr>
</tbody>
</table>

This experimental result demonstrates that the graphene electrode can be used as top floating plate in the AlN NPR technology. The ultra-reduced volume (single atomic monolayer) of the 2D graphene electrode enables higher operating frequency of the G-AlN NPR. However, the contaminated graphene electrode introduces extra load to the resonant system which negatively affects the performance of the G-AlN NPR. Cleaner and more effective protection of graphene during the XeF$_2$ isotropic etching is desired to achieve high quality graphene with lower electrode-introduced electrical loading, hence smaller resistance, $R_s$. 

*Table 2.3 Comparison between BVD model fitting parameters of the fabricated G-AlN NPR and the conventional AlN NPR*
2.4 2\textsuperscript{nd} Generation G-AlN NPR

In this section, an optimized 6-mask microfabrication process is introduced as a solution to the graphene quality degradation issue encountered during the implementation of the 1\textsuperscript{st} generation G-AlN NPRs. The resulting 2\textsuperscript{nd} generation G-AlN NPRs are the first to achieve high electromechanical performance comparable to conventional AlN NPRs despite mass and volume scaling and improved sensitivity.

The cause of the graphene degradation was experimentally identified to be the contamination introduced by the Shipley series photoresist employed to protect graphene during the etching steps. Therefore, different mask materials for graphene protection such as oxide, metals and polymers were explored and a thin-film called polydimethyl glutarimide (PMGI) polymer was selected based on experimental verification: PMGI was found to be an effective mask material for graphene and it did not cause contamination (no residues were observed after PMGI removal).

According to these findings, the device fabrication process was modified. The graphene layer transferred on top of the AlN NEMS die was patterned by oxygen plasma using PMGI as a mask. Furthermore, in order to avoid unintentional doping of the graphene layer during the final NEMS resonator release step in XeF\textsubscript{2} [29], PMGI was again deposited by spin coating on top of the graphene-NEMS die and properly patterned to protect the graphene electrodes. Finally, the G-AlN NEMS structure was released from the substrate by XeF\textsubscript{2} isotropic etching of Silicon and, after that, the PMGI protective layer was removed using a conventional photoresist solvent 1165.
The fabricated 2\textsuperscript{nd} generation G-AlN NPR is shown in optical microscope and SEM images below (Figure 2.12 and 2.13).

\textbf{Figure 2.12} Optical microscope images of a released 2\textsuperscript{nd} generation G-AlN NPR before (left) and after (right) the removal of PMGI

\textbf{Figure 2.13} SEM image of the fabricated G-AlN NPR and high magnification view of the anchor part which shows the boundary of the graphene plate. ($W=60\mu m$, $L=200\mu m$, $W_0=20\mu m$)
High quality graphene was maintained throughout the improved fabrication process as confirmed by Raman spectrum taken after release of the 2nd generation G-AlN NPR (Figure 2.14). The ~0.5 G-to-2D intensity ratio and a symmetric 2D band centered at ~2650 cm$^{-1}$ with a full width at half maximum of ~40 cm$^{-1}$ show typical feature of monolayer graphene [28].

![Raman spectrum of graphene taken on the fabricated G-AlN NPR after release process](image)

**Figure 2.14** Raman spectrum of graphene taken on the fabricated G-AlN NPR after release process

The fabricated 2nd generation G-AlN NPR was tested at room temperature and atmospheric pressure in a RF probe station and its electrical response was measured by an Agilent E5071C network analyzer after performing a short–open–load calibration on a reference substrate. The electromechanical performance of the device was extracted by Butterworth-Van Dyke (BVD) model fitting (Figure 2.15) and compared to the reference (Figure 2.16).
**Figure 2.15** Measured admittance and BVD fitting of the fabricated G-AlN NPR. \(C_0\) is the equivalent geometrical capacitance and \(R_m\) is the motional resistance.

**Figure 2.16** Measured admittances of the fabricated G-AlN NPR and the conventional AlN NPR.
Table 2.4 shows the comparison between the BVD model fitting parameters of the fabricated 2\textsuperscript{nd} generation G-AlN NPR and the reference device. Higher operating frequency and unchanged $k_t^2/Q$ was achieved with this particular 2\textsuperscript{nd} generation G-AlN NPR. Despite the ultra-reduced volume (single atomic monolayer), the 2D graphene electrode introduced only a relatively small and tolerable value of electrical resistance, $R_s$, compared to the 150 times thicker and 2500 times heavier gold electrode.

<table>
<thead>
<tr>
<th></th>
<th>$f_0$</th>
<th>$Q_m$</th>
<th>$k_t^2$</th>
<th>$C_0$</th>
<th>$R_m$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
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<td>281fF</td>
<td>189Ω</td>
<td>98Ω</td>
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<tr>
<td>G-AlN</td>
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<td>1001</td>
<td>1.81%</td>
<td>282fF</td>
<td>157Ω</td>
<td>228Ω</td>
</tr>
</tbody>
</table>

Table 2.4 Comparison between BVD model fitting parameters of the fabricated G-AlN NPR and the conventional AlN NPR

Furthermore, despite the reduced mass (~43%) and volume (~16%) and the increased sound velocity, hence resonant frequency (~23%), of the 2\textsuperscript{nd} generation G-AlN NPR, unchanged device figure of merit ($k_t^2/Q \approx 18$) compared to the conventional AlN NPR device was recorded. This experimental result demonstrates that the introduction of the graphene electrode not only enables the fabrication of AlN NPRs with lower volume and mass and improved sensitivity to mass loading but also, despite the volume scaling, allows the achievement of high values of $Q$ (~1000), which guarantee ultra-low noise performance of the sensor. The reduced mass and volume, and the increased frequency of operation of such G-AlN NPRs combined
with their high $Q$ factor values demonstrate the great potential of the proposed technology for the implementation of a new class of resonant sensors capable of achieving unprecedented values of limit of detection and detection speed.

It is worth noting that another fabricated G-AlN NPR showed higher $Q$ than the reference device (Figure 2.16, 2.17 and Table 2.5). The effective device area of this G-AlN NPR was $75 \, \mu m \times 200 \, \mu m$ ($W \times L$), the pitch, $W_0$, of bottom Platinum (Pt) finger electrode was $25 \, \mu m$, resulting in a high order contour-extensional mode resonator working at high resonance frequency of $192$ MHz. Despite a bottom metal interdigital electrode is still employed in this G-AlN NPR, increased $Q$ was firstly observed due to the smaller electrode damping and interface strain introduced by graphene top electrode.

![Figure 2.16 Measured admittance and BVD fitting of another fabricated G-AlN NPR](image)

$Q = 911$

$k_t^2 = 1.98\%$

$C_o = 410 fF$

$R_m = 138 \Omega$
Figure 2.17 Measured admittance and BVD fitting of the reference corresponding to the G-AlN NPR shown above

<table>
<thead>
<tr>
<th></th>
<th>$f_0$</th>
<th>$Q_m$</th>
<th>$k_i^2$</th>
<th>$C_0$</th>
<th>$R_m$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>161MHz</td>
<td>728</td>
<td>1.86%</td>
<td>413fF</td>
<td>218Ω</td>
<td>135Ω</td>
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<tr>
<td>G-AlN</td>
<td>192MHz</td>
<td>911</td>
<td>1.98%</td>
<td>410fF</td>
<td>138Ω</td>
<td>233Ω</td>
</tr>
</tbody>
</table>

Table 2.5 Comparison between BVD model fitting parameters of the fabricated G-AlN NPR and the corresponding conventional AlN NPR for reference
2.5 Temperature Coefficient of Frequency for G-AlN NPR

The thermal stability of a resonator is determined by its temperature coefficient of frequency (TCF) which indicates the sensitivity of the device resonant frequency to temperature variations. The TCF of the fabricated G-AlN NPRs was measured and found to be $-30$ ppm/$^\circ$C (Figure 2.18). This value is comparable to what is typically measured in conventional AlN based MEMS resonators [10], which is dominant by the temperature-dependent Young's modulus of AlN.

It is worth noting that graphene absorbs a fixed 2.3% of the illumination passing through it over a wide range of wavelengths (300 - 2500nm) and this absorption is a linear function of the number of layers (<10 layers) [30-32]. So the combination of high sensitivity to temperature, high thermal isolation (due to the fact that the nano plate is released from the silicon substrate) and the unique optical absorption properties of graphene shows great potential of the proposed G-AlN NPR technology for the implementation of a new class of ultra-fast and sensitive IR./THz detector [3].
Figure 2.18 Temperature coefficient of frequency (TCF) measurement of the G-AlN NPR
3. SINGLE TRANSISTOR

OSCILLATOR BASED ON G-ALN NPR

This section presents the first demonstration of a high frequency (245 MHz) single transistor oscillator based on the 2nd generation G-AlN NPR. For the first time, a 2D electrically conductive graphene layer was integrated on top of an ultra-thin (500 nm) AlN nano-plate and excited into a high frequency contour-extensional mode of vibration by piezoelectric transduction. The resulting ultra-thin, low mass and high frequency G-AlN nanomechanical resonator showed high values of electromechanical coupling coefficient ($k_t^2 \approx 1.8\%$) and quality factor ($Q_m \approx 1000$) which enabled the implementation of a low phase noise (-87 dBc/Hz @ 1kHz offset and -125 dBc/Hz floor) single transistor oscillator. The experimental results also demonstrate the great potential of the proposed technology for the implementation of a new class of ultra-sensitive and low noise G-AlN resonant sensors.

3.1 Pierce Oscillator Circuits

The Pierce oscillator is a type of electronic oscillator particularly well-suited for use in piezoelectric crystal oscillator circuits. The circuit can be implemented using a minimum of components: a single inverting amplifier, two resistors, two
capacitors, and the MEMS/NEMS resonator, which acts as a highly selective filter element (Figure 3.1) [33]. The low manufacturing cost of this circuit, and the outstanding frequency stability, give it an advantage over other designs of resonator readout circuits.

The Printed Circuit Board (PCB) was designed using Altium Designer and fabricated by Advanced Circuits, Inc. The pierce oscillator circuits were assembled with soldering tools and electronic components bought from Digi-Key. Both of the 2\textsuperscript{nd} generation 245MHz G-AlN NPR and a 178MHz conventional AlN NPR based on the same core design but employing a 150 nm thick gold top electrode instead of the 2D graphene top electrode were directly wire-bonded to pierce oscillator circuits implemented with an ATF-551M4 E-pHEMT GaAs transistor. (Figure 3.1)

![Figure 3.1 Oscillator circuit](image)
3.2 Phase Noise Performance

The electromechanical performance of the 2nd generation 245MHz G-AlN NPR was compared to a 178MHz conventional AlN NPR, fabricated on the same substrate and based on the same core design but employing a 150 nm thick gold top electrode instead of the 2D graphene top electrode (Figure 3.2 and Table 3.1).

![Figure 3.2 Measured admittances and BVD fitting of the fabricated G-AlN NPR and the conventional AlN NPR](image)

Table 3.1 shows the comparison between the BVD model fitting parameters of the fabricated G-AlN NPR and the conventional AlN NPR. Higher operating frequency and comparable $k_i^2 Q_{load}$ was achieved with the G-AlN NPR. Despite the
relatively high sheet resistance (~1.5kΩ/□) of the in-house synthesized graphene layer, the 2D graphene electrode introduced only a relatively small and tolerable value of electrical resistance, $R_s$, compared to the 250 times thicker and 3750 times heavier gold electrode. It is worth noting that much lower sheet resistance (~60 Ω/□) can be achieved in commercially available graphene [34] which would further reduce the electrical loading of the graphene electrode to < 2% of the total loss of the system.

$$f_0 Q_{load} k_t^2 C_0 R_m R_s$$

<table>
<thead>
<tr>
<th></th>
<th>$f_0$</th>
<th>$Q_{load}$</th>
<th>$k_t^2$</th>
<th>$C_0$</th>
<th>$R_m$</th>
<th>$R_s$</th>
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<tbody>
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<td>1.90%</td>
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<tr>
<td>G-AlN</td>
<td>245MHz</td>
<td>408</td>
<td>1.81%</td>
<td>282fF</td>
<td>157Ω</td>
<td>228Ω</td>
</tr>
</tbody>
</table>

*Table 3.1 Comparison between BVD model fitting parameters of the fabricated G-AlN NPR and the conventional AlN NPR based on the same core design but employing a 150 nm thick gold top electrode*

The phase noise was measured for best bias conditions using an Agilent N9010A EXA signal analyzer. Despite the 250 fold smaller volume of the top electrode and the 38% higher operating frequency, improved phase noise performance was recorded for the G-AlN device due to its higher mechanical $Q$ ($Q_m$≈1000) (Figure 3.3).
This experimental result demonstrates that the introduction of the graphene electrode not only enables the fabrication of AlN NPRs with lower volume and mass and improved sensitivity to mass loading but also, despite the volume scaling, allows the achievement of high values of $Q_m$, which guarantees ultra-low noise performance of the oscillator readout. The reduced mass and volume, and the increased frequency of operation of such G-AlN NPRs combined with their high $Q$ factor values demonstrate the great potential of the proposed technology for the implementation of a new class of resonant sensors capable of achieving unprecedented values of limit of detection and detection speed.

*Figure 3.3 Measured phase noise of the two oscillators*
4. CONCLUSIONS

4.1 Summary

In this thesis, a high frequency (245 MHz) Graphene-Aluminum Nitride (G-AlN) nano plate resonator (NPR) was designed, fabricated and tested. For the first time, a 2-dimensional electrically conductive graphene layer was integrated on top of an ultra-thin (500 nm) AlN nano plate and excited into a high frequency contour-extensional mode of vibration by piezoelectric transduction. Despite the reduced mass (~43%) and volume (~16%) and the increased sound velocity, hence resonant frequency (~23%), of the G-AlN NPR, unchanged device figure of merit ($k_t^2 Q \approx 18$) was recorded compared to one of the conventional AlN NPRs, fabricated on the same substrate and based on the same core design but employing a 100 nm thick gold top electrode instead of the 2D graphene top electrode. The achieved high electromechanical performance of the ultra-thin, low mass and high frequency G-AlN nanomechanical resonator enabled the implementation of a low phase noise (-87 dBc/Hz @ 1kHz offset and -125 dBc/Hz floor) single transistor oscillator.

These experimental results demonstrate that reliable electrical transduction of high frequency mechanical vibration in an ultra-thin and low-mass G-AlN nano plate is possible and can be employed for the making of a new class of resonant sensors with improved sensitivity and noise performance, hence with unprecedented detection capabilities.
4.2 Future Work

The research work presented in this thesis has set the pathway for the development of a new class of ultra-sensitive and low noise G-AlN gravimetric sensors. The 2D graphene electrode not only represents the thinnest and lightest conductive electrode ever used to excite vibration in a piezoelectric NEMS resonator but it also has the potential to be used as an effective chemical interactive material with the largest possible surface to volume ratio. For example, it has been reported that graphene can directly absorb gas molecules such as NH₃, CO, NO₂ and H₂O [35], and it also can be functionalized to work as a chemical sensor by using single stranded DNA as a sensitizing agent which is capable of sensing Dimethyl methylphosphonate (DMMP) or other Chemical Warfare Simulants (CWS) [36]. The author strongly believes that with the commercially available lower sheet resistance graphene (~60 Ω/□), the in developing metal-free G-AlN NPR technology and the unique property of graphene mentioned above, ultimately scaled NEMS piezoelectric resonator (<10 nm) and ultra-sensitive gravimetric sensors with unprecedented detection capabilities (<zg/μm²) can be achieved in the near future.
Reference


