Multilayer graphene condenser microphone

Dejan Todorović1,2, Aleksandar Matković3, Marijana Milićević1,4, Djordje Jovanović4, Radoš Gajić4, Iva Salom1 and Marko Spasenović4

1 School of Electrical Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11120 Belgrade, Serbia
2 Dirigent Acoustics Ltd, Mažuraničeva 29/9, 11050 Belgrade, Serbia
3 Center for Solid State Physics and New Materials, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia
4 Institute Mihailo Pupin, University of Belgrade, Volgina 15, 11060 Belgrade, Serbia
5 Present Addresses: Laboratoire de Photonique et Nanostructures, LPN/CNRS, Route de Nozay, 91460 Marcoussis, France

E-mail: spasenovic@ipb.ac.rs

Keywords: graphene, acoustics, nanomechanics, microphones, membrane

Supplementary material for this article is available online

Abstract
Vibrating membranes are the cornerstone of acoustic technology, forming the backbone of modern loudspeakers and microphones. Acoustic performance of a condenser microphone is derived mainly from the membrane’s size, surface mass and achievable static tension. The widely studied and available nickel has been a dominant membrane material for professional microphones for several decades. In this paper we introduce multilayer graphene as a membrane material for condenser microphones. The graphene device outperforms a high end commercial nickel-based microphone over a significant part of the audio spectrum, with a larger than 10 dB enhancement of sensitivity. Our experimental results are supported with numerical simulations, which also show that a 300 layer thick graphene membrane under maximum tension would offer excellent extension of the frequency range, up to 1 MHz.

Introduction
Graphene has emerged as an exciting new material for fundamental research and novel applications, due to its many remarkable properties such as ultrahigh carrier mobility [1], high optical transparency [2, 3], and enormous chemical reactivity [4]. Furthermore, graphene shows record high thermal conductivity [5] and a Young’s modulus of 1 TPa [6], making it a durable thin membrane. Measurements have shown that monolayer graphene has a breaking strength of 42 N m⁻¹ which is over 200 times greater than a hypothetical steel film of the same thickness [6]. Multilayer graphene membranes in particular are useful for a wide range of applications, including thermal interface engineering [7], broadband light absorption [8], and high-conductance electrodes [9].

Graphene membranes are lightweight, and their mechanical properties promise remarkable possibilities even in fields as demanding as optomechanics [10, 11]. Although electrical and optical properties of graphene have been extensively studied and applied, and their mechanical properties are a burgeoning field of research [12], the first utilizations of the mechanical properties of graphene in acoustics have only recently been realized, with the first demonstrations of a graphene thermoacoustic device [13, 14], electrostatic loudspeaker [15] and a graphene earphone [16, 17].

Vibrating lightweight membranes are of tremendous relevance in the acoustic industry, as exemplified by the reign of condenser microphones as the best platform for recording and measuring acoustic waves using the same pressure detection principle as the human ear, with high quality, repeatable and predictable performance [18]. Condenser microphones, discovered at Bell Labs in 1916, utilize a vibrating membrane as one plate of a capacitor charged by a polarization voltage. Incident acoustic waves set the membrane in motion, which is detected with an attached electronic circuit. Most improvements to condenser microphones in the last three decades focused on the electronics, for example on improving the analogue to digital converters and placing them inside the microphone body to minimize interference and noise in analogue signal transmission chain. An exception is the rise of microphones based on...
Our sample consists of multilayer microelectromechanical systems (MEMS), typically using thin silicon as the membrane material [19]. MEMS-based microphones offer the advantage of small size, which is important for applications in hearing aids and aeroacoustic arrays [20]. MEMS microphones feature membranes with a thickness on the order of 1 μm and have shown a frequency response similar to conventional macroscopic microphones [21]. The nanoscale thickness of graphene membranes and their exceptional mechanical properties make them an excellent candidate for even smaller microphones with enhanced spectral response.

Here we report an experimental realization of a condenser microphone with a multilayer graphene membrane with performance comparable to a professional microphone, at a membrane thickness of only 25 nm. Packaged in the same commercial casing and using the same electronic amplifier, the graphene microphone sensitivity outperforms a professional microphone (Brüel & Kjaer (B&K) 4134) by 12 dB, at frequencies up to 11 kHz. The experimental data are supported with numerical simulations, which additionally show that a membrane consisting of 300 layers of graphene would respond in a usable frequency range extending up to 1 MHz, in the ultrasonic part of the spectrum.

**Sample fabrication and experimental details**

Our sample consists of multilayer (thickness ~60 layers) graphene grown on nickel foil with chemical vapour deposition (CVD, Graphene Platform). Fabrication from CVD graphene ensures consistent quality across the sample range and is at the moment the most viable solution [22] for potential large scale production of graphene microphones. The nickel is etched away in a 40 mg ml⁻¹ iron chloride water solution, yielding a floating multilayer graphene film (figure 1(a)). The graphene film is scooped out of the solution onto a supporting polyethylene terephthalate frame which has a circular hole in the center (figure 1(b)). The graphene covers the hole to form the membrane. The diameter of the hole and membrane was varied between 5 mm and 12 mm with similar results. The membrane is subsequently left to dry for 24 h prior to mounting the device into the microphone casing (figures 1(c) and (d)). This fabrication procedure results in a high yield of membranes, at a success rate larger than 70%. To increase the yield, the membranes were not rinsed in water or other solvents [6], as surface tension causes the membrane to break at the lines that form at boundaries of the original nickel domains. Leaving out the rinsing step, a residue of iron chloride is left on the membrane, as confirmed with scanning electron microscopy (see supporting information, figure S2). The residue does not appear to significantly affect the performance of the microphone, as demonstrated in the following paragraphs. Raman spectroscopy was used to confirm that the membrane consists of graphene (supporting information, figure S4). Atomic force microscopy of membranes indicated an average thickness of 25 nm (supporting information, figure S6). Membranes survived in open air for periods between several hours and days (supporting information). A lifetime on the order of several days is typical for nanomembranes and could possibly be extended by the addition of thin layers of strengthening materials on top of the membrane. Such additions would, however, come at the expense of mechanical flexibility [23]. Furthermore, in the case of membranes made of graphene,
which is one of the strongest materials known, it is not obvious what material to use as the strengthener.

Results and discussion

The graphene microphone was used to record a conversation, which gave a good subjective impression (supporting information). Quantitatively, microphone performance is measured by recording a constant amplitude sine sweep from 10 Hz to 24 kHz, played on a small loudspeaker. The signal was amplified with a professional microphone preamplifier (B&K ZC0032) and analysed with a PrismSound dScope Series III signal generator and analyser. The comparison (results in figure 2) and substitution (result in figure 4) methods were used to compare several graphene microphones against the professional microphone (details are given in the supplementary information). During the measurements a dc polarization voltage of 200 V was applied to the microphones. Frequency response of the small loudspeaker at 90° incidence with the professional and graphene microphone is presented in figure 2.

The distance between the membrane and the oppositely charged condenser back plate was crudely controlled by tightening and loosening the holder screw (see supplementary information). The microphone sensitivity increases as the membrane approaches the back plate, down to a minimal distance of 18.6 μm allowed by the microphone casing. The membrane static tension is estimated using the membrane collapse effect [24, 25] as:

$$T_{\text{m}0} = \sigma t = \frac{27\varepsilon_0 r^2 V_p^2}{64h^3} \left[ \frac{\text{N}}{\text{m}} \right]$$

where σ is membrane tensile stress (Nm⁻²), t is membrane thickness (m), ε₀ is dielectric permittivity of air, r is radius of membrane (m), Vp is polarization voltage (V) and h is nominal distance from diaphragm to back plate (m).

For a polarization voltage of 200 V and a membrane radius of 5 mm, the estimated static tension is approximately 640 N m⁻¹.

The static tension on the graphene membrane is five times smaller than the manufacturer specified tension on the nickel membrane of the professional microphone. A small static tension results in a large microphone efficiency, as in [26]:

$$M = \frac{V_p r^2}{8hT_{\text{m}0}} \left[ \frac{\text{V}}{\text{Pa}} \right]$$

and is hence the most likely reason for the superior performance of the graphene microphone. The trade-off of low membrane tension is a low cutoff frequency f_max given as [27]:

$$f_{\text{max}} = \frac{2.4}{2\pi\varepsilon_0\sigma_m} \sqrt{\frac{T_{\text{m}0}}{\sigma_m}},$$

where σ_m is surface mass density of membrane (kg m⁻²).

However, the graphene membrane has a surface mass density three orders of magnitude smaller than that of the nickel membrane of the professional microphone, which compensates for the weak tension.

To reinforce the experimental results and explore the limits of graphene microphone membranes, we employ finite element method (FEM) calculations. We start from the well-known publicly available professional condenser microphone model in Comsol Multiphysics⁶.

Two different models were employed, a simplified 2D axial model of the condenser microphone (figure 3(a)) and a detailed 3D symmetric model of the professional condenser microphone (figures 3(b) and (c)). As is the case in the experiment, the full 3D model (figures 3(b) and (c)) contains an air-filled volume below the electrode and a vent to equalize the static pressure between the microphone and the environment. The simplified 2D model (figure 3(a)) does not

⁶ B&K 4134 Model for COMSOL.
include the air-filled volume and thus ignores any acoustic pressure on the back of the electrode. This simplified model has shown to be faithful to the experimental result in a recent demonstration of a graphene microphone [28]. Both the simplified 2D and full 3D model invoke several COMSOL physics interfaces: Thermoacoustics, Electrostatics, Moving Mesh, and a Membrane model. The acoustic response of the microphone is solved with full coupling of these four interfaces, using the COMSOL frequency-domain linear perturbation solver. The models include the polarization (‘pull-in’ voltage) and the resulting deformation of the membrane, which defines the zeroth order linearization point. The dimensions and parameters of the simulation are given in table S1 (supplementary information).

Simulations were performed for three cases: the original professional microphone (membrane material is 5 μm thick nickel foil, with applied static tension of 3160 N m⁻¹); the experimentally measured 60-layer graphene membrane microphone; and a ¼' microphone with a hypothetical 300-layer graphene membrane (see supporting information). The simulated response spectrum of the 60-layer graphene microphone membrane, compared to the measured microphone response, is depicted in figure 4. The normalized results, in agreement with the measurements, indicate that the graphene microphone has sensitivity higher than the professional condenser microphone by more than 11 dB, up to a frequency of 11 kHz. At higher frequencies, the higher static tension of the professional microphone’s nickel membrane starts to dominate, leading to a reduced relative performance of the graphene microphone, both in simulation and experiment. Furthermore, the performance of the graphene microphone at high frequencies is adversely affected by the supporting metal adapter which was built to fit the graphene membrane into the commercial casing. The frequency response and sensitivity in the limit of thin membranes are defined by the geometry and membrane static tension, and air load on the membrane dominates the mass of the membrane. In this limit, it is interesting to simulate slightly thicker graphene membranes, which could theoretically support a higher static tension. Experimentally, higher tension could be achieved by tightening the membrane holder during the fabrication, or by optimizing the membrane drying conditions, although in practice, for thin membranes, it has proven to be difficult to find this optimum point beyond which the membrane breaks due to excess tension.

The strength of a graphene membrane scales linearly with the number of layers [29]. In accordance with equation (3), membranes that support a larger static tension have higher cutoff frequencies. Figure 5 depicts simulated response of a 300 layer graphene membrane (red line), under the same experimental conditions achieved in the rest of this work. The microphone exhibits superb performance over a wide frequency range, up to 1 MHz. The microphone sensitivity at frequencies below 100 kHz remains comparable to the small membrane professional condenser extended range microphones (B&K 4136 and B&K 4138). At frequencies larger than 100 kHz, the simulated 300 layer graphene microphone response stays constant, while the sensitivity of the two professional
microphones (dashed and dashed dotted lines in figure 5) drops sharply.

In conclusion, we demonstrate multilayer graphene microphones with a performance comparable to professional microphones. A microphone with a 60 layer graphene membrane displays up to 15 dB higher sensitivity compared to a commercial microphone, at frequencies up to 11 kHz. Finite element simulations confirm graphene microphone sensitivity and cutoff, and indicate that a microphone with a 300 layer graphene membrane would show similar sensitivity as state of the art condenser microphones, but with a frequency range extended up to 1 MHz, deeply entering the ultrasonic part of the spectrum. Our work paves the way for the use of widely available and inexpensive graphene in acoustics and touches upon the important ultrasound part of the spectrum, unreachable by the conventional state of the art microphones. Further improvements in graphene production quality will be a crucial benefit to the design of large membrane multilayer graphene microphone and its applications.

Author Contributions
DT and IS conceived the experiment. AM and MM prepared the samples. DT, AM, DJ, MM and MS performed the measurements. All authors together discussed the results and wrote the manuscript. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Acknowledgments
This work was supported by Dirigent Acoustics Ltd and the Serbian Ministry of Education and Science under projects OI171005, III45018 and TR32038.

References
[1] Geim A K and Novoselov K S 2007 Nat. Mater. 6 183–91
[2] Nair R R, Blake P, Grigorenko A N, Novoselov K S, Booth T J, Stauber T, Peres N M R and Geim A K 2008 Science 320 1308
[3] Bonaccorso F, Sun Z, Hasan T and Ferrari A C 2010 Nat. Photonics 4 611–22
[4] Denis P A and Iribarne F 2013 J. Phys. Chem. C 117 19048–55
[5] Balandin A A 2011 Nat. Mater. 10 569–81
[6] Lee C, Wei X, Kysar J W and Hone J 2008 Science 321 385
[7] Shahil K M F and Balandin A A 2012 Nano Lett. 14 861–7
[8] Obraztsov P A, Rybin M G, Tyurnina A V, Garnov S V, Obraztsova E D, Obraztsov A N and Svirko Y P 2011 Nano Lett. 11 1540–5
[9] Kuroda M A, Tersoff J, Newns D M and Martyna G J 2011 Nano Lett. 11 3629–33
[10] Song X, Oksanen M, Li J, Hakonen P J and Sillanpää M A 2014 Phys. Rev. Lett. 113 027404
[11] Singh V, Bosman S J, Schneider B H, Blanter Y M, Castellanos-Gomez A and Steele G A 2014 Nat Nanotechnology 9 820–4
[12] Galiotis C, Otakar F, Koukaras E N and Sfyris D 2015 Annu. Rev. Chem. Biomol. Eng. 6 6.1–6.20
[13] Suk J W, Kirk K, Hao Y, Hall N A and Rouff R S 2012 Adv. Mater. 24 6342–7
[14] Fei W, Zhou J and Guo W 2015 Small 11 2252–6
[15] Zhou Q and Zettl A 2013 Appl. Phys. Lett. 102 223109
[16] Tian H, Yang Y, Li C, Mi W T, Mohammad M A and Ren T L 2015 RSC Adv. 5 17366–71
[17] Tian H, Li C, Mohammad M A, Cui Y L, Mi W T, Yang Y, Xie D and Ren T L 2014 ACS Nano 8 5883–90
[18] B&K 1996 Microphone Handbook vol 1 (Naerum: Bruel and Kjaer)
[19] Bay J, Hansen O and Bouwstra S 1996 Sensors Actuators A 53 232–6
[20] Liu J, Martin D T, Kadirvel K, Nishida T, Cattafesta L, Sheplak M and Mann B P 2008 J. Sound Vib. 309 276–92
[21] Iguchi Y, Goto M, Iwaki M, Ando A, Tanioka K, Tajima T, Takeshi F, Matsunaga S and Yasuno Y 2007 Sensors Actuators A 135 420–5
[22] Zurrutxa A and Marinelli C 2014 Nat. Nanotechnology 9 730–4
[23] Brenckle M A, Cheng H, Hwang S, Tao H, Paquette M, Kaplan D L, Rogers J A, Huang Y and Omenetto F G 2015 ACS Appl. Mater. Interfaces 7 19870–5
[24] Kaajakari V 2009 Practical MEMS: Design of Microsystems, Accelerometers, Gyroscopes, RF MEMS, Optical MEMS, and Microfluidic Systems (Las Vegas, NV: Small Gear Publishing)
[25] Schomburg W K 2011 Introduction to Microsystem Design vol 1 (Berlin: Springer)
[26] Kinsler L 1982 Fundamentals of Acoustics. (New York: Wiley)
[27] Zukerwar A 1994 Principles of operation of condenser microphones chapter 3AIP Handbook of Condenser Microphones ed G Wong and T Embleton (New York: AIP Press)
[28] Zhou Q, Zheng J, Onishi S, Crommie M F and Zettl A K 2015 Proc. Natl Acad. Sci. 112 8942–6
[29] Lee J-H, Loya1 P E, Lou J and Thomas E L 2014 Science 346 1092–6