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Electrostatically Actuated Membranes of Cross-Linked Gold Nanoparticles: Novel Concepts for Electromechanical Gas Sensors †

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Abstract: We report the preparation of freestanding membranes of cross-linked gold nanoparticles (GNPs) and demonstrate their application as electromechanical sensors for volatile organic compounds (VOCs). First, we show that the fundamental vibrational mode frequency of electrostatically excited GNP-membranes shifts significantly when exposing them to solvent vapors. We attribute this effect mainly to the reduction of the membranes' pre-stress. Second, the relief in pre-stress upon analyte sorption can also be detected via quasi-static actuation of the membranes. In this case, the increase of the deflection amplitudes at constant bias voltages can be measured as the sensor signal and correlated to the analyte's concentration. Additionally, we propose a facile route to the fabrication of such hybrid MEMS/NEMS sensors using layer-by-layer spin-coating and contact printing.

Keywords: gold; nanoparticle; membrane; electrostatic; actuator; resonator; sensor; gas sensor; MEMS; NEMS

1. Introduction

Substrate-supported films of ligand-stabilized or cross-linked gold nanoparticles (GNPs) have shown great potentials for applications as chemiresistors and strain gauges. For example, their use in medical diagnosis and integration into wearable electronics has been demonstrated [1]. Recently, freestanding GNP-membranes gained considerable attention and current research activities explore their fundamental electromechanical properties as well as their application as actuators and highly sensitive sensors [2–4]. In previous works we studied the application of α,ω-alkanedithiol cross-linked GNP-membranes as electrostatically driven actuators [5] and resonators [6]. When exposing such resonators to solvent vapors at reduced total pressure we observed a significant decrease of their resonance frequency, suggesting that such devices may find applications as novel types of highly sensitive electromechanical chemical sensors [7]. Thus, the objective of our present study was to explore the responses of freestanding GNP-membranes to solvent vapors by monitoring their fundamental resonance frequency under reduced total pressure whilst applying an AC drive voltage or, alternatively, by measuring their deflection amplitudes at ambient pressure when applying DC voltages. Furthermore, we devised a facile and robust route to the fabrication of such sensors based on depositing cross-linked GNP-films by spin-coating and transferring them onto 3D-structured electrodes via contact printing.

2. Materials and Methods

Dodecylamine stabilized GNPs with core diameters of 3–4 nm were synthesized according to the literature [8]. Thin films of 1,6-hexanedithiol cross-linked GNPs were deposited by our standard spin-coating procedure onto glass substrates [9]. For the fabrication of the sensor devices these films were detached from their original substrates and transferred onto 3D-structured substrates, which were equipped with gold electrodes. These substrates were structured using standard photo-lithography, either to prepare square cavities within a ~10 μm thick SU-8 layer deposited onto a thermally oxidized silicon wafer (device A), or to etch trenches into a thermally oxidized silicon wafer (device B) [6,7]. In case of device A the back electrode was deposited onto the oxidized silicon wafer before depositing and structuring the SU-8 layer. The top electrode was then deposited onto the SU-8 layer. In case of device B the p-type doped silicon substrate itself was used as the back electrode and the top electrode was deposited onto the thermally grown oxide layer. For transferring the cross-linked GNP-films onto these 3D-structured substrates two different methods were used. The first approach is based on detaching the cross-linked GNP-film from the original substrate by flotation on water [5,6]. The detached film remained floating at the water surface and could be transferred onto the sensor substrate using the Langmuir-Schaefer technique. After drying, a freely suspended membrane covering the cavity in the SU-8 layer was obtained (device A). According to the second approach, the freestanding GNP-membranes were produced via contact printing. Here, the cross-linked GNP-film was first scratched to produce a stripe pattern, covered with a thin sacrificial PMMA-layer, and then detached from the original substrate using a PDMS-stamp, similar as described by Li et al. [10]. Afterwards, the GNP-film was stamped onto the sensor substrate using a procedure similar to that reported by Choi et al. [11]. After carefully removing the stamp, freely suspended GNP-membranes spanning the trench of the 3D-stuctured substrate were obtained (device B). Finally, the sacrificial PMMA-layer was removed by mild solvent treatment.

The morphology, thickness and conductivity of the cross-linked GNP-films were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), and current-voltage (IV-) measurements. To study the electromechanical responses of the freestanding GNP-membrane to solvent vapors the sensor (device A) was placed into a test cell, which was connected to a rotary vane pump for adjusting the overall cell pressure and to a commercial gas calibration system (MCZ Umwelttechnik GmbH, CGM 2000) for providing solvent vapors at various concentrations. Nitrogen 5.0 was used as zero gas. During the measurements the freestanding GNP-membrane was actuated electrostatically at ambient temperature either by applying DC voltage pulses ranging from 20 to 100 V (quasi-static actuation) or by applying an AC sine function voltage with an amplitude of 5 V (dynamic actuation). During AC actuation an offset DC voltage of 10 V was applied to avoid zero-crossing of the net voltage and, hence, of the electrostatic forces acting on the freestanding membrane. The deflection amplitudes of the membrane and its resonance frequency were measured using a laser interferometer (Nanovibration Analyzer NA, SIOS GmbH) directed at the center of the membrane. The experimental setup and procedures are described in detail elsewhere [7].

3. Results

Panels (a) and (b) in Figure 1 show schematic drawings of the two sensors (devices A and B) fabricated and characterized in this study. The GNPs used for membrane preparation had average diameters of 3–4 nm. As shown by the representative TEM image in panel (c) the GNP-membranes consisted of a granular network of GNPs with feature sizes determined by the sizes of the particles. The GNP-membrane used for the fabrication of device A had a thickness of ~39 nm and a conductivity of ~0.13 $\Omega^{-1}cm^{-1}$. Panel (d) in Figure 1 shows an SEM image of device B with four GNP-membranes bridging a trench of ~35 μm width. The membranes were transferred onto the substrate using a PDMS-stamp. Thus, this result evidences the feasibility of fabricating freestanding membranes of cross-linked GNPs via facile contact printing.

Panel (e) in Figure 1 shows the shifts of the fundamental resonance frequency f_0 (~0.35 MHz) of device A when dosed with toluene vapor (1000, 4000, 7000, 10,000 ppm) at a constant total pressure of 20 mbar. The sensor responded fully reversible with a frequency decrease of up to −11 kHz, i.e.,

−3% of f_0. Finally, panel (f) in Figure 1 shows the central point deflection of the membrane (device A) measured under ambient pressure (~1 bar) when applying DC voltage pulses in the range 20 to 100 V. These measurements reveal that the deflection amplitudes increase significantly in the presence of toluene vapor and that this effect becomes much more pronounced when increasing the toluene concentration from 1000 to 10,000 ppm.

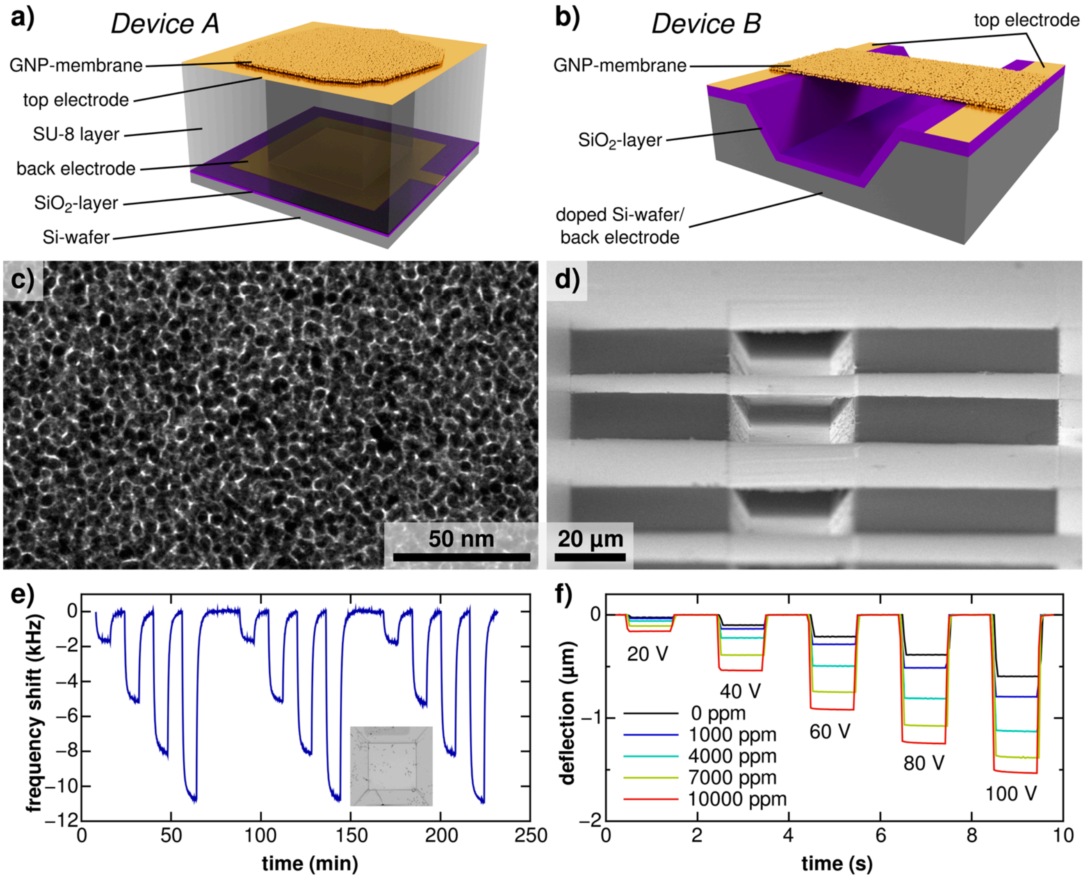

Figure 1. (**a**) Sensor with square cavity defined in an SU-8 resist layer (device A). The cavity is covered by the cross-linked GNP-membrane; (**b**) Sensor having an open bridge structure (device B). The GNP-membrane spans a trench etched into a silicon substrate; (**c**) Representative TEM image of the cross-linked GNP-membrane; (**d**) SEM image of freestanding GNP-membranes spanning a trench etched into a silicon substrate; (**e**) Shifts of the fundamental resonance frequency of sensor device A when dosed with toluene vapor (1000, 4000, 7000, 10,000 ppm) at a total pressure of 20 mbar. Inset: Optical microscopy image of the GNP-membrane. The edge length of the square cavity was ~100 µm; (**f**) Membrane deflections measured when actuating sensor device A by applying DC voltage pulses with and without the presence of toluene vapor, as indicated.

4. Discussion

In this study we demonstrated the application of an electrostatically driven actuator based on a freestanding membrane of cross-linked GNPs as electromechanical sensor for the detection of VOCs. Previously, we assigned the decrease of the fundamental resonance frequency of GNP-membrane resonators observed upon sorption of solvent molecules to the reduction of the membrane's pre-stress and concluded that the gravimetric effect is negligible [7]. Here, we confirmed this interpretation by studying the quasi-static deflection of a GNP-membrane (device A) by applying DC voltages in the absence/presence of toluene vapor. Taking into account the membrane's dimensions, the deflection amplitude, and the applied electric field it is possible to calculate the change in pre-stress due to analyte sorption, revealing a decrease from ~14 MPa to lower than ~5 MPa when toluene vapor was present at the highest concentration (10,000 ppm). Importantly, the quasi-static actuation mode can be applied at ambient pressures while the dynamic operation mode, i.e., the measurement of the resonance frequency shift, can only be applied at reduced pressure in order to avoid significant damping of membrane's vibration.

Furthermore, we demonstrated a facile route to the fabrication of such sensors by transferring the GNP-membrane, which was prepared by a simple spin-coating process, onto the sensor substrate via contact printing (device B). In contrast to previously reported methods, which are based on transferring the GNP-membrane from a water surface, contact printing allows for spatial control of the transfer process and is even suited for controlling the pre-stress of the resulting freestanding GNP-membrane.

Currently, we focus on characterizing the chemical selectivity and sensitivity of membrane-based electromechanical sensors. Further, we will replace the interferometer by implementing a simplified optical or full electrical detection of the membrane's deflection. Finally, together with other previous studies [1], our findings presented above suggest the possibility of designing advanced chemical sensors based on freestanding GNP-membranes with multimode optical, resistive, and electromechanical signal transduction mechanisms.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. Segev-Bar, M.; Bachar, N.; Wolf, Y.; Ukrainsky, B.; Sarraf, L.; Haick, H. Multi-Parametric Sensing Platforms Based on Nanoparticles. *Adv. Mater. Technol.* **2017**, *2*, 1600206.
2. Wang, Y.; Kanjanaboos, P.; McBride, S.P.; Barry, E.; Lin, X.-M.; Jaeger, H.M. Mechanical properties of self-assembled nanoparticle membranes: Stretching and bending. *Faraday Discuss.* **2015**, *181*, 325–338.
3. Schlicke, H.; Rebber, M.; Kunze, S.; Vossmeyer, T. Resistive pressure sensors based on freestanding membranes of gold nanoparticles. *Nanoscale* **2016**, *8*, 183–186.
4. Gauvin, M.; Grisolia, J.; Alnasser, T.; Viallet, B.; Xie, S.; Brugger, J.; Ressier, L. Electro-mechanical sensing in freestanding monolayered gold nanoparticle membranes. *Nanoscale* **2016**, *8*, 11363–11370.
5. Schlicke, H.; Battista, D.; Kunze, S.; Schröter, C.J.; Eich, M.; Vossmeyer, T. Freestanding Membranes of Cross-Linked Gold Nanoparticles: Novel Functional Materials for Electrostatic Actuators. *ACS Appl. Mater. Interfaces* **2015**, *7*, 15123–15128.
6. Schlicke, H.; Schröter, C.J.; Vossmeyer, T. Electrostatically driven drumhead resonators based on freestanding membranes of cross-linked gold nanoparticles. *Nanoscale* **2016**, *8*, 15880–15887.
7. Schlicke, H.; Behrens, M.; Schröter, C.J.; Dahl, G.T.; Hartmann, H.; Vossmeyer, T. Cross-Linked Gold-Nanoparticle Membrane Resonators as Microelectromechanical Vapor Sensors. *ACS Sens.* **2017**, *2*, 540–546.
8. Leff, D.V.; Brandt, L.; Heath, J.R. Synthesis and Characterization of Hydrophobic, Organically-Soluble Gold Nanocrystals Functionalized With Primary Amines. *Langmuir* **1996**, *12*, 4723–4730.
9. Schlicke, H.; Schröder, J.H.; Trebbin, M.; Petrov, A.; Ijeh, M.; Weller, H.; Vossmeyer, T. Freestanding films of crosslinked gold nanoparticles prepared via layer-by-layer spin-coating. *Nanotechnology* **2011**, *22*, 305303.
10. Li, H.; Wu, J.; Huang, X.; Yin, Z.; Liu, J.; Zhang, H. A Universal, Rapid Method for Clean Transfer of Nanostructures onto Various Substrates. *ACS Nano* **2014**, *8*, 6563–6570.
11. Choi, M.K.; Park, I.; Kim, D.C.; Joh, E.; Park, O.K.; Kim, J.; Kim, M.; Choi, C.; Yang, J.; Cho, K.W.; et al. Thermally Controlled, Patterned Graphene Transfer Printing for Transparent and Wearable Electronic/Optoelectronic System. *Adv. Funct. Mater.* **2015**, *25*, 7109–7118.