Graphene-Gold Electrodes for Flexible Nanogenerators Based on Porous Piezoelectric PVDF Films

M. Fortunato[1,2], A. Rinaldi[1,2], A. Tamburrano[1,2], G. De Bellis[1,2], T. Dikonimos[3], N. Lisi[3], and M.S. Sarto[1,2]
[1]Dept. of Astronautical, Electrical and Energy Engineering (DIAEE), Sapienza University of Rome, via Eudossiana 18, Rome 00184, Italy, email: marco.fortunato@uniroma1.it
[2]Res. Center for Nanotech. Applied to Eng. of Sapienza (CNIS), Sapienza Univ. of Rome, P.le Aldo Moro, 5, Rome 00185, Italy
[3]ENEA Casaccia Research Center, via Anguillarese 301, Rome 00123, Italy

***Abstract*—**In this work, we develop graphene-gold electrodes (GGEs) for flexible nanogenerators made of porous piezoelectric PVDF films. The bilayer electrode structure was conceived in order to avoid the short circuit between top and bottom electrodes produced through direct Au sputtering over the film surface. Gold was sputtered over chemical-vapor-deposition (CVD) grown graphene film, that was subsequently transferred onto a PVDF film. We analysed the morphology and electrical properties of GGEs with increasing Au thickness in order to optimize the electrode surface conductivity and to guarantee high flexibility. The piezoelectric coefficient d_{33} of PVDF films and GGE-topped PVDF films were investigated through Piezoresponse Force Microscopy (PFM). We observed that the obtained values of d_{33}, with and without GGEs, are in agreement with each other. This result allows to directly correlate the nanoscale piezoelectric properties to macroscale piezoelectric properties. Furthermore, a flexible nanogenerator made by a PVDF film top- and bottom-contacted with the bilayer GGEs was measured using a commercial mini-shaker. The obtained results are in good agreement with the measured d_{33} of the uncontacted PVDF film, obtained through PFM.

I. INTRODUCTION

In recent years flexible nanogenerators have attracted a considerable interest for application in smart textiles, medicine and battery-free nodes of wireless sensors networks for the internet of things [1]. Piezoelectric polymers, such as the Poly(vinylidene fluoride) [PVDF; $(CH_2CF_2)_n$] are considered as suitable candidates to fabricate such devices. PVDF has attracted much attention for its chemical resistance, thermal stability, high mechanical strength, large remnant polarization, short switching time and significant electrical properties [2-4]. A critical issue in the fabrication of flexible nanogenerators is the electrical bonding of the piezoelectric material through flexible electrodes. Graphene has been shown to be an excellent electrode for nanogenerators devices, due to its extraordinary electrical and mechanical properties, combined with a good flexibility [5]. Nevertheless, graphene makes the top contact very delicate and its adhesion to PVDF has yet to be tested in depth. Moreover, the sheet resistance of graphene remains still too high, around few 100 Ω/□ [6], to have a low-resistance electrode. For the aforementioned reasons, in this work, we investigated the feasibility of using graphene-gold electrodes (GGEs) to guarantee high flexibility and high electrical conductivity. Actually, we observed that the direct sputtering of gold electrodes over the surface of porous PVDF can be challenging, due to the fact that the sputtered gold diffuses through the polymer film and produces a short circuit between the top and bottom electrodes. To avoid these short circuits, we used graphene as an interlayer between the polymer and the sputtered gold. In our work we used an organic compound, namely cyclododecane, to assist the transfer of the gold/graphene films [6]. We characterized both the morphology and the electrical properties of three different graphene-gold bilayer electrodes, made with sputtered gold layers of three different thicknesses (80, 50 and 30 nm). We investigated the piezoelectric properties of the PVDF films with and without GGE through Piezoresponse Force Microscopy (PFM). PFM is a very effective technique to characterize the piezo electric properties of materials at the nanoscale. PFM allows the study of the local sample strain generated by the applied electric field with a lateral resolution of a few nanometers [2, 7-9]. PFM is a versatile and non-invasive method to investigate the piezoelectric response of ferroelectric materials without the need for an elaborate sample preparation. For comparison purposes, the macroscopic piezoelectric response (i.e. the piezoelectric coefficient d_{33}) of a flexible nanogenerator, with top and bottom bilayer electrodes structure, was characterized, by using a commercial mini-shaker

II. MATERIALS AND METHODS

A. Production of PVDF Films

PVDF films were prepared by dissolving 5 wt% of PVDF powder (Solef 6010, Solvay Specialty Polymers, having molecular weight of 300,000-330,000 g/mol) in 20 ml of a solvent mixture consisting of dimethylformamide (DMF) and acetone (1:1 v/v). A clear and transparent solution was obtained upon continuous stirring at room temperature for 3 h, ensuring the complete dissolution of PVDF. The solution was casted onto a clean glass plate and subsequently placed in an oven at 100°C for 12 h for the complete evaporation of the solvent. Finally, the obtained films, having thickness of approximately 15 µm each, were peeled off the substrate (see Fig. 1).

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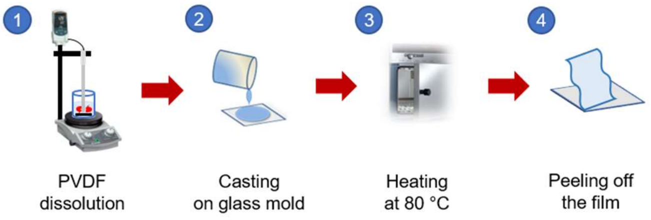

Fig. 1. Preparation of PVDF films.

B. *Production of Graphene-Gold Electrodes*

Few layer graphene (FLG) films were grown on copper foils (25 µm thick) at 1070 °C in an inductively heated furnace by the Chemical Vapor Deposition (CVD) of ethanol (C_2H_5OH) at low pressure (8 mbar). The samples were previously annealed in Ar/H_2 (20/20 sccm) for 10 min at the same temperature. Three different gold layers: 80, 50 and 30 nm, were then sputtered on as-synthesized FLG coated copper foils. After removing the graphene grown on the back of the sample by oxygen plasma treatment, gold-graphene-copper substrates were spin-coated with cyclododecane as support layer. The substrates were treated in an etching solution of ammonium persulfate (APS) and deionized water (200 g/l) to remove the copper foil, and then rinsed in deionized water to eliminate any Cu and etch bath residues. The gold/graphene/cyclododecane films were finally scooped from the rinsing bath using the desired substrate and transferred onto the previously obtained PVDF film (see section A); cyclododecane was finally removed by heating at 65°C (see Fig. 2) [6].

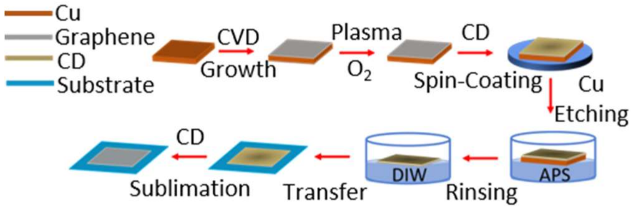

Fig. 2. Preparation route of Few layer of graphene (FLG).

C. *Morphological and Electrical Characterizations*

The morphology of the graphene-gold electrodes was observed using a Field Emission Scanning Electron Microscope (FE-SEM, Zeiss Auriga) operated at an accelerating voltage of 5 kV, and an Atomic Force Microscope (Bruker-Veeco, Dimension Icon) operated in tapping mode.

The sheet resistance of the graphene-gold films transferred onto SiO_2 or PVDF substrates was measured by the four-point probe method in a controlled environment at constant temperature (23±0.5°C) and humidity (35±5%), using a Keithley 6221 dc/ac current source and a Keithley 2182a nano-voltmeter [6]. Voltamperometric tests were also performed to evaluate the dc resistance between the top and bottom electrodes.

The piezoelectric coefficient (d_{33}) of the final device, consisting of a PVDF film sandwiched between top and bottom bilayer electrodes, was tested using a commercial mini-shaker (Sinocera, YE2730A) operated with a force of 0.25 N and with a frequency of 110 Hz.

D. *Piezoresponse Force Microscopy (PFM) Characterization*

The piezoelectric response was evaluated using PFM (Dimension Icon, Bruker-Veeco). This technique is based on the standard contact mode AFM setup [7]. In addition to the AFM setup, an alternating voltage is applied to the sample through the tip, while grounding the bottom electrode. In this work, the PFM measurements were performed under the following conditions: silicon cantilever (Bruker) with 5 N/m nominal spring constant, resistivity of 0.01-0.025 Ωcm and 150 kHz nominal resonance frequency. The samples were glued on a metal plate through silver paint. In order to measure the piezoresponse of the samples, an a.c. voltage was applied with amplitude varying from 0 V to 10 V, in 2 V-steps at a constant frequency of 15 kHz. Scan rate and scan area were 0.5 Hz and (500×500) nm^2, respectively [2].

III. RESULTS AND DISCUSSIONS

A. *Morphology*

FE-SEM images of neat PVDF, PVDF topped by graphene and PVDF topped by a graphene-gold electrode are shown in Fig. 3(a), (b), and (c), respectively. AFM images and corresponding height profiles of the same samples are show in Fig. 2(a)-(b), (c)-(d) and (e)-(f).

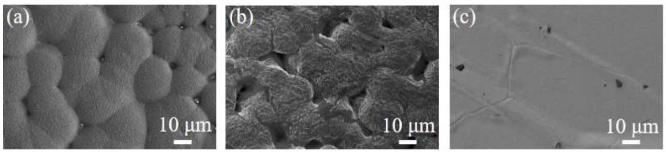

Fig. 3. FE-SEM image of neat PVDF (a), PVDF with graphene only (b) and PVDF with graphene-gold electrode (c).

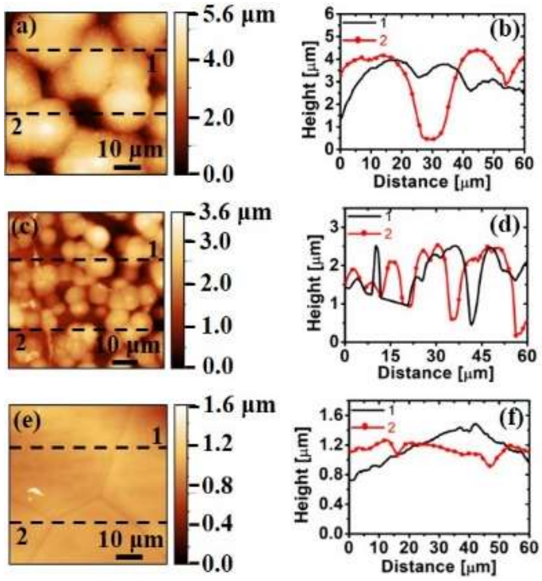

Fig. 4. AFM topography in tapping mode and height profile along the black lines for neat PVDF (a)-(b), PVDF with graphene (c)-(d) and PVDF with graphene-gold electrode (e)-(f).

The surface of the neat PVDF is characterized by a classic spherulitic structure. The morphology seems not to be altered by the presence of graphene. On the contrary, the roughness of the sample is highly affected by the topmost gold layer morphology.

B. *Electrical properties*

Flexibility and sheet resistance of the bilayer electrode can be in general tuned by modifying the thickness of the gold layer. The measured sheet resistance of the GGEs transferred on PVDF and, for sake of comparison, on Si/SiO$_2$ are reported in Table 1.

Table 1 Measured sheet resistance of the graphene-gold electrodes transferred on PVDF and on Si/SiO$_2$.

Sample	**R$_s$ (Ω/□)**	
	Si/SiO$_2$	**PVDF**
FLG + Au 80 nm	0.40	0.41
FLG + Au 50 nm	0.55	1.23
FLG + Au 30 nm	0.71	1.02

The insulation resistance tests carried on samples having the top electrode made of either a single gold layer or graphene-gold bilayer have shown opposite results. In the former case, we measured resistances of a few Ohms, indicating that the top and bottom electrodes are in electrical contact. In the latter case we measured resistance values higher than 100 GΩ, demonstrating good electrical insulation between the two electrodes.

C. *Piezoelectric response*

Using a standard contact mode AFM setup and applying an alternating voltage to the sample it is possible to perform PFM measurements. A photodiode detects the deformation of the cantilever that is equal to the sample deformation. A lock-in amplifier (LIA) separates the topography and piezoresponse signal [2]. The LIA allows to measure, even small signals, (like average displacements of just a few picometers), with a high signal-to-noise ratio, (pm). A calibration factor has been used to convert the raw amplitude signal, measured using the quadrant photodiode and LIA, in to the displacement amplitude. Three-dimensional topography and the piezoelectric contrast, scanning an area of (500×500) nm^2, are reported in Fig. 5. Since the piezoelectric contrast does not directly correlate with the topography [10], the piezoelectric effect is due to intrinsic piezoelectric properties of the materials and not originated from the cross-talk with the topographic signal.

PFM measurements were performed on 3 different regions for each sample (scanning area (500×500) nm^2) to evaluate the average piezoelectric properties of the samples. In Fig. 6 we report the average values of displacement as a function of the amplitude of the applied a.c. voltage.

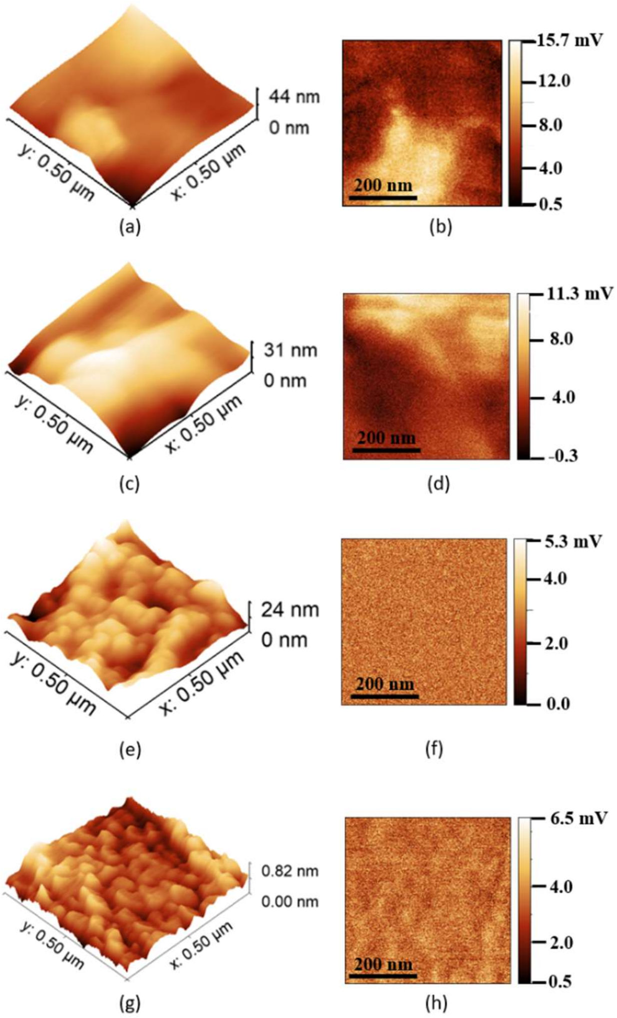

Figure 6 Three-dimensional topography and domain contrast of PFM at 10 V of PVDF without GGEs (a)-(b), of PVDF with GGEs with 30 nm of gold (c)-(d), of PVDF with GGEs with 50 nm of gold (e)-(f) and of PVDF with GGEs with 80 nm of gold (g)-(h).

In agreement with the theory of the converse piezoelectric effect, we obtained a linear behavior of the piezoelectric response as a function of the applied voltage. According to Eq. (1) the displacement (Δz) depends linearly upon the applied voltage amplitude (V_{ac}) and the angular coefficient is the piezoelectric coefficient (d_{ij}):

$$d_{ij} = \Delta z / V_{ac} \tag{1}$$

In our experiment the voltage is applied along the vertical axis, so that the measured piezoelectric coefficient is d_{33}. We estimated the value of d_{33} of the uncontacted and coated PVDF films using a reference sample, consisting of periodically poled lithium niobate (PPLN), purchased from Bruker. Since the piezoelectric coefficient of the PPLN sample is $d_{33} = 7.5$ pm/V, it is possible to determine the calibration parameter α, from the slope of the piezoresponse amplitude vs applied voltage, using the following equation:

$$A_{piezo} = \alpha \cdot d_{33} \cdot V_{ac} \tag{2}$$

where A_{piezo} is the amplitude of the measured piezoresponse of the calibration sample, measured in volt, and V_{ac} is the applied voltage. We then apply again Eq. (2) in order to estimate the value of d_{33} of the sample under test, using the value of α, obtained from Eq. (2) applied to the calibration sample, and the A_{piezo} value measured for the sample under test over an area of

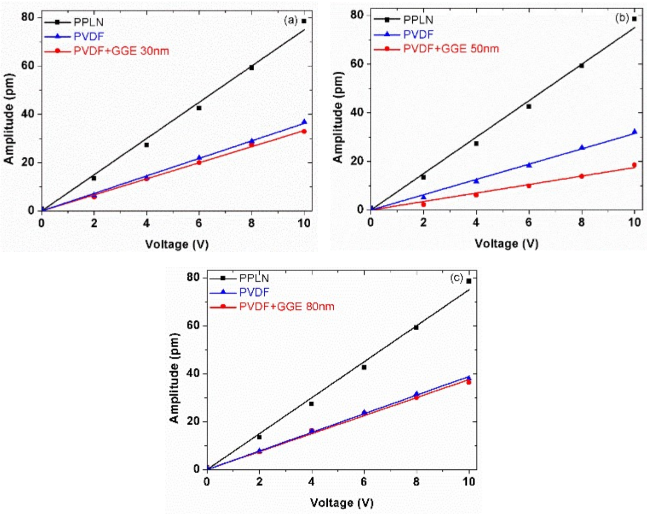

Fig. 5. Measured piezoelectric signal, averaged over three different areas, versus the amplitude of the applied a.c. voltage. Comparison between PVDF and PVDF plus GGE with 30 nm of gold (a), PVDF and PVDF plus GGE with 50 nm of gold (b), PVDF and PVDF plus GGE with 80 nm of gold (c).

Table 2 Piezoelectric coefficient evaluated by averaging the PFM signal over 3 different areas each of (500x500) nm^2.

Sample	**Δd$_{33}$ (pm/V)**
PVDF+GGE 30 nm	0.30 ± 0.03
PVDF+GGE 50 nm	1.40 ± 0.62
PVDF+GGE 80 nm	0.12 ± 0.01

(500x500) nm^2, corresponding to the amplitude of the applied a.c. voltage V_{ac} [11]. The difference between the d$_{33}$ obtained over the sample with and without the GGEs are reported in Table 2.

The d$_{33}$ measured over the sample with the GGE showed a slightly lower value if compared with the value measured over the samples without the top electrode. This behavior is more evident for the GGE with 50 nm of Au. We suppose that this is due to the non-perfected adhesion of the top electrode with the PVDF films, that as said remains one of the thing that has yet to be tested in depth. Since for all the three bilayer electrode structures we found an excellent flexibility, we finally adopted the thickest graphene-gold electrode, that showed the lowest value of sheet resistance both on the Si/SiO$_2$ and on the PVDF, to fabricate a flexible nanogenerator. In order to produce the flexible nanogenerator we decided to use the PVDF film that showed the highest value of d$_{33}$ (8.30±3.35) pm/V. Then we performed d$_{33}$ measurements using a commercial mini-shaker with a force of 0.25 N at the frequency of 110 Hz. We obtained a value of (9.00±0.45) pm/V which is in good agreement with the one (8.30±3.35) pm/V measured through the Piezoresponse Force Microscopy technique (PFM) on the same PVDF film without electrodes.

IV. CONCLUSIONS

We present a possible solution to realize flexible electrodes with high electrical properties for nanogenerators based on porous piezoelectric PVDF films. We demonstrate that bilayers composed of graphene-gold are able to avoid short circuit between the top and bottom electrodes and guarantee, at the same time, low sheet resistance and high flexibility. We verified the quality of our GGE measuring the d$_{33}$, through PFM, over the neat PVDF films and over the PVDF films topped by a GGE electrode. The measured d$_{33}$ over PVDF with and without GGE are found to be in good agreement with each other. This behavior allows us to say that our local characterization with PFM is a good representation of the global piezoelectric properties of our samples. The lowest value, obtained for the GGE with 50 nm of Au, is believed to be due to the low adhesion between the PVDF film and the top electrode. Furthermore, in this work, we verified the quality of our device (using our best PVDF film with top and bottom GGEs) measuring the d$_{33}$ through the use of a commercial mini-shaker. The obtained value of (9.00±0.45) pm/V pm/V, is in very good agreement with the value obtained through the PFM (8.30±3.35) pm/V, without electrodes.

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