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(Article begins on next page)

# A novel electrolyte gated graphene field effect transistor on cyclo olefin copolymer foil

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**Abstract**— In this work an electrolyte gated Graphene field effect transistor (G-FET) has been developed exploiting a Hot-embossing assisted technique to transfer Single Layer Graphene (SLG) on a Cyclo Olefin Copolymer (COC) foil. An investigation on the processing and materials related effects has been carried out by a comparison with a more traditional Poly(methyl methacrylate) (PMMA) transfer approach. The fabricated G-FETs were tested as pH sensors and the electrical characteristics were investigated.

**Keywords**— Graphene, CVD, Graphene transfer, flexible electronics, Hot Embossing, G-FET

## I. INTRODUCTION

Graphene based field effect transistors (G-FET) are arising as novel high performing biosensors that exploit single layer or few layers of graphene (SLG or FLG) to detect biomolecules as DNA or proteins at very low concentration [1]–[3]. The sensitivity of this kind of sensors and hence the limit of detection (LOD) is highly influenced by the SLG quality. In order to produce high quality graphene, the most effective method is Chemical Vapor Deposition (CVD) on Cu or Ni foils [4] and then the transferring on an insulator layer containing the patterned electrodes. Critical aspects have been reported in literature concerning the transferring procedure [5], which consists in the spinning of Poly(methyl methacrylate) (PMMA) on the Cu foil (graphene side), the etching of the Cu foil, the deposition on the device substrate and the final PMMA removal. The graphene layer is prone to degradation from step to step, and residual contamination of PMMA leads to n-type doping [6] that negatively affects the sensors performance. Therefore, alternative methods for SLG transfer are needed especially when the substrates are flexible and the complexity of handling and processing increases. Hot embossing technique has been successfully employed to transfer micro patterns obtained by a photolithographic step [7], [8], moreover is a well known effective process to implement nano-imprinting lithography [9], [10]. In this work, a comparison between two completely different transferring methods was carried out to investigate the effects on the device characteristics. More in details, a hot embossing transfer process of SLG was developed to obtain a novel flexible G-FET on a Cyclo Olefin Copolymer (COC) foil. This method allows transferring the SLG without the PMMA sacrificial layer, reducing the graphene processing steps. In this paper a focus on this new approach with respect to a more

traditional fabrication one was reported. For this purpose, G-FET pH sensors on Si/SiO<sub>2</sub> and COC substrates have been fabricated and compared.

## II. EXPERIMENTAL

### A. Graphene growth and G-FET fabrication

SLG has been grown with a Moorfield NanoCVD-8G on 2 cm x 2 cm Cu foils. The Cu was previously rinsed in HCl in order to remove the native oxide from the surface.

Two different transferring procedures were exploited in order to obtain the final devices. The devices were then used to investigate the influence of these transferring steps on their performances.

A Ti/Au (10/100 nm) film was evaporated on a 140 μm thick COC foil and on a 4" Si/SiO<sub>2</sub> wafer (Fig. 1, step a1 and b1). The source and drain electrodes were defined by photolithography with AZ 1518 resist followed by wet etching of the Ti/Au layer (Fig. 1, step a2-a3 and b2-b3). The obtained channel is 30 μm long and 2 mm wide.

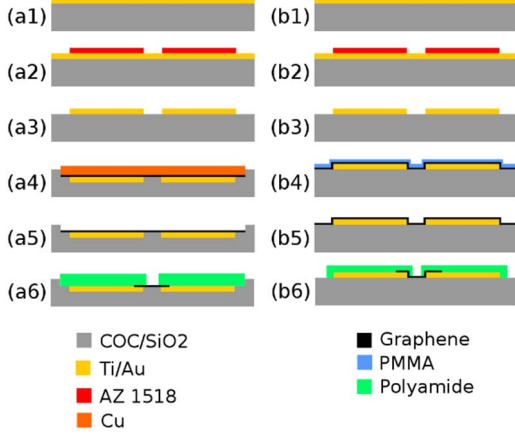
The first transfer procedure employed the hot embossing technique (Fig. 1, step a4). The Cu foil with the SLG was embossed on the COC foil with the following parameters (model HEX01 JENOPTIK Microtechnik): 80 °C process temperature, 10000 N of applied force for 60 s. Cu was then etched in a FeCl<sub>3</sub> solution for 20 min, leaving the SLG on the Au electrodes (Fig. 1, step a5). The yield of the transfer process was 87.50% (seven devices properly working out of the eight fabricated).

In the second transfer procedure PMMA sacrificial layer was used. A layer of PMMA (1.35% in anisole) was spin coated on the Cu foil in order to cover the SLG. The Cu was then etched in a FeCl<sub>3</sub> solution. The graphene/PMMA foil was cautiously rinsed with deionized water (DI) to get rid of the etchant and placed on the substrate (either COC or Si/SiO<sub>2</sub>) (Fig. 1, step b4). After graphene transfer the devices were vacuum dried at R.T. in order to minimize PMMA contamination [11]. PMMA was then removed in acetone, leaving only the SLG on the substrate with the electrodes (Fig. 1, step b5). The yield of the PMMA assisted transfer was 68.75% with eleven working devices out of the sixteen fabricated.

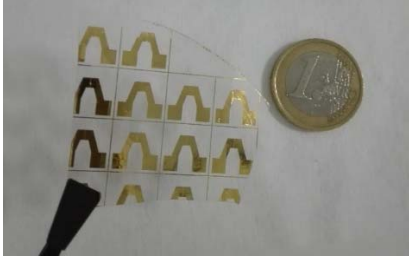
After the transfer, graphene was patterned by photolithography (AZ 1518 photoresist) and 30 s oxygen plasma

to connect source and drain electrodes only in the channel region.

Finally, the source and drain electrodes were passivated with polyamide (Asahi Kasei AM-271) to prevent short circuits of the devices during electrolyte gating (Fig. 1, step a6 and b6). The fabricated devices on COC substrate are shown in Fig 2.



**Figure 1:** G-FET fabrication process flow via hot embossing (a1-a6) and common PMMA assisted transfer (b1-b6).



**Figure 2:** G-FET devices fabricated via hot embossing process of SLG on COC.

### B. Electrical Characterization and pH sensing

The electrical characterization has been performed with a Keysight B2912A Source/Measure unit on three sets of devices differing by the graphene transfer method or the substrate. The characterized G-FETs were respectively: fabricated via PMMA assisted transfer on Si/SiO<sub>2</sub> substrate, fabricated via PMMA assisted transfer on COC foil, and fabricated via hot embossing on COC foil.

The devices were mounted on the probe station and a PDMS well with 50  $\mu$ l capacity was placed on the transistors and filled with the electrolyte. An Ag/AgCl leak free reference electrode was placed inside the PDMS well to apply the gate potential.

Device trans-characteristics have been measured in DI water at fixed drain voltage (20, 40, 60, 80 and 100 mV) sweeping the gate potential between -1 V and +1 V. The leakage current through the gate was constantly monitored and always at least four orders of magnitude lower than the drain current.

The pH response of G-FETs fabricated on Si/SiO<sub>2</sub> and G-FETs fabricated via hot embossing on COC were then investigated. Phosphate buffered saline at physiological concentration (PBS 1x, Sigma Aldrich) was used as gate

electrolyte. This buffer allowed to investigate a pH range and ionic strength interesting for biological applications. Starting from pH 7.4 of the stock solution, buffers with pH ranging between 6.4 and 8.2 were obtained adding small amount of HCl or NaOH. pH values were measured before the sensing experiments with a VWR SB70B pH-meter.

### III. RESULTS AND DISCUSSION

The G-FETs on the Si/SiO<sub>2</sub> and on COC were fabricated following the described processes to have a clear view of the influence of the transferring method on the electrical characteristic. PMMA assisted transfer was used both on the Si/SiO<sub>2</sub> substrate and COC to verify the effects introduced by the polymer with respect to commonly used materials. The liquid-gated G-FETs show the typical ambipolar characteristics (Fig. 3). The transfer characteristics present a V-shaped p- to n-type transition for all the tested devices.

Transfer with PMMA on COC results in G-FETs with a Dirac point close to the one obtained on Si/SiO<sub>2</sub>, thus meaning that no significant charging effects are shown (Fig. 3a and Fig.4a). Nevertheless, the transferring process with PMMA on COC is trickier due to the flexible substrate and the possible fracture of the graphene layer reduces the overall final conductance and the maximum trans-conductance (Fig. 4b).

Graphene embossed on COC shows a Dirac point comparable to the PMMA transferred one both on COC and Si/SiO<sub>2</sub> (Fig. 4a). The trans-conductance of embossed SLG is higher than the one of PMMA-transferred SLG on the polymeric substrate, and comparable to the one obtained on Si/SiO<sub>2</sub> (Fig. 4b).

The field effect mobilities of charge carriers have been calculated as [12]:

$$\mu_{e/h} = \frac{g_{m_{e/h}} L}{V_{ds} W C_{TG}} \quad (1)$$

Where the top gate capacitance  $C_{TG}$  is the series connection of the EDL capacitance ( $C_{EDL} \approx 18 \mu F \cdot cm^{-2}$  [13]) and graphene quantum capacitance ( $C_Q \approx 2 \mu F \cdot cm^{-2}$  [14]). The obtained  $\mu_{e/h}$  are shown in Table 1.

**Table 1:** Transconductances ( $g_{m_{e/h}}$ ) and field effect mobilities ( $\mu_{e/h}$ ) for electrons and holes extrapolated from the I-V transfer characteristics, and measured pH sensitivities (S).

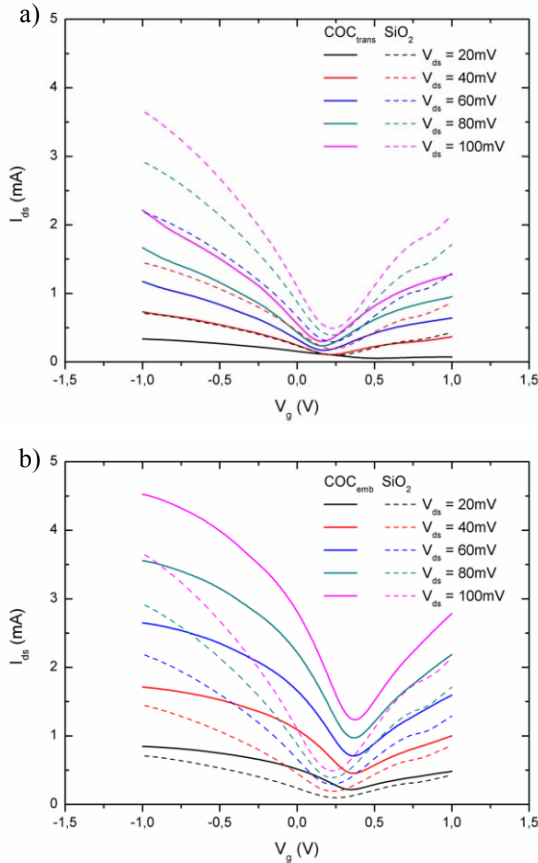
Device	$g_{m_e}$ (mS)	$g_{m_h}$ (mS)	$\mu_e$ $\left(\frac{cm^2}{V \cdot s}\right)$	$\mu_h$ $\left(\frac{cm^2}{V \cdot s}\right)$	S $\left(\frac{mV}{pH}\right)$
COC <sub>emb</sub>	1.70	2.67	141	221	42
COC <sub>trans</sub>	1.05	1.72	87	142	-
Si/SiO <sub>2</sub>	2.15	2.81	178	233	28

pH sensing experiments have been performed in high ionic strength buffer (PBS 1x, ionic strength  $\approx 162.7$  mM) with the COC-embossed G-FET and the PMMA transferred on Si/SiO<sub>2</sub> G-FET showing higher transconductance. Both the devices have

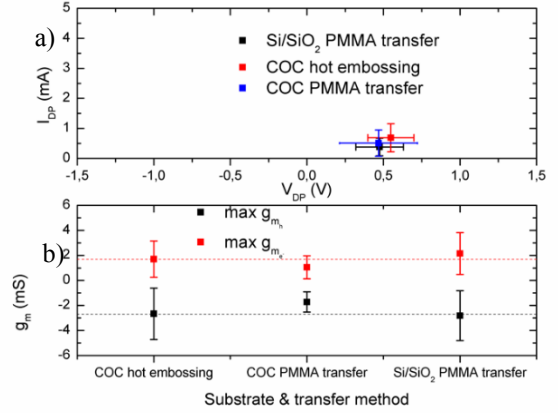
been able to detect pH variation as low as  $\Delta\text{pH} = 0.2$  in the range 6.4-8.2 (Fig. 5). The pH range has been chosen in order to stay within the buffering range of PBS (pH 5.8 - 8.0) [15]. Wider pH range may be explored using different buffers. The obtained calibration curves for both devices are shown in Fig. 6. These calibration curves demonstrate COC-embossed G-FET has performances comparable to PMMA transferred G-FET on Si/SiO<sub>2</sub>. The pH sensitivity  $S$  (see Table 1) extracted from the shift of  $V_{DP}$  for the COC-embossed G-FET ( $S_{COC} \approx 42 \text{ mV}/\text{pH}$ ) is 50% higher than the one obtained for the PMMA-transferred on Si/SiO<sub>2</sub> G-FET ( $S_{Si} \approx 28 \text{ mV}/\text{pH}$ ), and the latter is consistent with values found in the literature [16].

#### IV. CONCLUSION

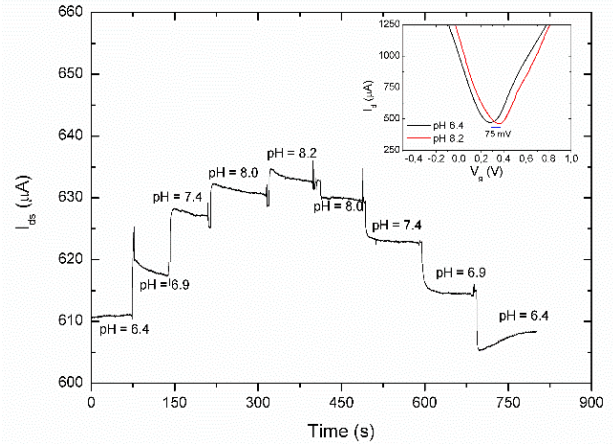
In conclusion, a novel G-FET on COC flexible substrate graphene has been developed using an innovative transfer method based on the hot embossing technique. This method allows maintaining the same sensing performances of the G-FET on Si/SiO<sub>2</sub> substrate using a traditional approach. This hot embossing method has the advantage to skip the commonly used but time-consuming PMMA-assisted transfer, paving the way for the industrial scaling of high quality CVD grown graphene transfer on flexible substrates.



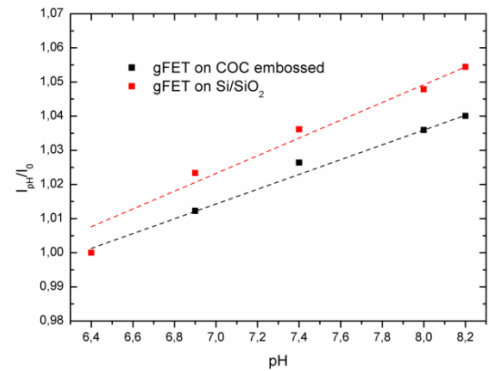
**Figure 3:** Comparison of  $I_{\text{drain}}$  vs  $V_{\text{gate}}$  characteristics in DI water at fixed drain voltage of a) G-FET fabricated via PMMA assisted transfer on Si/SiO<sub>2</sub> and COC substrates; b) G-FET fabricated via PMMA assisted transfer on Si/SiO<sub>2</sub> and via hot embossing on COC.



**Figure 4:** a) Comparison of the Dirac point (Dirac voltage  $V_{DP}$ , Dirac current  $I_{DP}$ ) for the three different sets of devices at fixed  $V_{ds} = 100 \text{ mV}$ ; b) Max hole transconductance ( $g_{mh}$ ) and electron transconductance ( $g_{me}$ ) for the three sets of devices at  $V_{ds} = 100 \text{ mV}$ .



**Figure 5:** pH sensing at high ionic strength (PBS 1x used as pH buffer) performed with G-FET fabricated via hot embossing on COC. Inset: shift of the trans-characteristic due to a pH variation from 6.4 to 8.2.



**Figure 6:** pH calibration curve for G-FET fabricated via PMMA transfer on Si/SiO<sub>2</sub> and via hot embossing on COC. The current has been normalized with respect to the value at pH 6.4 in order to allow a direct comparison between different devices.

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