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# Resistive switching in graphene-organic device: Charge transport properties of graphene-organic device through electric field induced optical second harmonic generation and charge modulation spectroscopy

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ABSTRACT

Graphene-based resistive random access memory devices is a promising non-volatile memory technology that combines low operation voltage and power, extremely fast write/erase speeds, excellent reliability and storage capacity of RRAM with low-cost, large area and flexibility of carbon-based technologies. However, low-cost single-step synthesis of high-quality graphene remains a challenge. In this paper, high quality graphene synthesized directly from sustainable carbon source (*M. alternifolia* oil) was used as electrode and pentacene/$C_{60}$ as active layers in carbon-based RRAM. I-V measurements were used to demonstrate reproducible switching (rapid increase in current) at certain voltage which was reversible. Charge transport and accumulation was visualized using electric field induced optical second harmonic generation and charge modulation spectroscopy. Hole transport from graphene layer to the organic layer was the primary cause of the observed switching behavior.



## 1. Introduction

There is growing demand for novel nonvolatile memory technology compatible with low-cost, large-area, and energy-efficient flexible electronics applications. Resistive random access memory (RRAM) has emerged as the next generation nonvolatile memory device technology due to its simple structure, high operation speed, high scalability, and multibit storage potential. RRAM is based on resistance change modulated by electrical stimulus, where high (HRS) and low (LRS) resistive states can be read non-destructively.

Resistive switching characteristics have been demonstrated in a wide variety of solid-state materials, including solid electrolytes, perovskites, binary transition metal oxides, and amorphous silicon [1,2]. Although devices based on metal oxide thin films have suitable combination of fast switching speed, scalability, and low-power consumption, their specific material characteristics make them unsuitable for use over large-area flexible or temperature-sensitive substrates.

RRAM devices based on carbon materials, including organic semiconductors [3], amorphous carbon [4] and graphene oxide [5,6] have also been demonstrated. The advantages of using carbon-based materials include lower fabrication costs, printability, and simple device structures [7]. Furthermore, if non-volatile memory can be realized in carbon, the logic and memory devices can be integrated on a same carbon-based platform as carbon-based field effect transistors.

With its unrivalled combination of electrical, mechanical, thermal and optical properties [7–10], graphene has been investigated as a promising electrode material for organic semiconducting and memory devices [11,12], with graphene-pentacene devices showing rectifying properties. The switching characteristics of organic RRAM devices are strongly influenced by the properties of interfaces, in particular the interface state between an electrode and an organic material as it defines the charge injection barrier,

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conduction mechanism, and bulk resistance [3]. However, high yield fabrication of quality graphene is expensive and is typically associated with very high process temperatures, use of hazardous chemicals, metallic catalysts, as well as lengthy and complex chemical synthesis procedures [7]. Thus, significant scientific and commercial efforts have been directed towards the development of more economical, efficient, and environment- and human-health-friendly approaches for graphene synthesis [8,13].

In this paper, we report on the single-step fabrication of high-quality large-area graphenes from natural non-toxic *M. alternifolia* oil vapor [14], and demonstrate a distinctive resistive switching property in graphene-organic semiconductor interfaces produced using oil-derived graphenes. Fabricated devices, such as graphene/α–NPD/Alq3, graphene/pentacene, graphene/$C_{60}$ and graphene/pentacene/$C_{60}$ devices, are interrogated using the Electric Field Induced Second Harmonic Generation and Charge Modulation Spectroscopy to explain the observed resistive switching phenomena.

## 2. Experiments

### 2.1. Graphene fabrication

Plasma-enhanced chemical vapour deposition (PECVD) was used for the fabrication of graphene. The experimental system consists of a custom made quartz tube reactor with heater wound on the quartz tube. A variable voltage controller was used to obtain the temperature of 800 °C. The base pressure of 0.05 mbar was initially obtained. $H_2$ gas was flown at the rate of 30 sccm and the system pressure was adjusted to 0.20 mbar. The RF energy from the *Navio* RF Generator operating at 13.56 MHz frequency through the *Navio* Matching Network was coupled to the reactor using capacitive coupling. The system was optimized for an input RF energy of 500 W and reactor tube temperature of 800 °C. Silicon substrates with 100 nm oxide layer were pretreated with plasma for 1 min for surface preparation and cleaning. The vapors of *Melaleuca alternifolia* oil were then introduced into the system using a flow controller.

*M. alternifolia* oil is a non-synthetic source of carbon. *M. alternifolia* essential oil is a plant-derived precursor rich in carbon compounds such as terpinen-4-ol ($C_{10}H_{18}O$, 30–48%), γ-terpinene ($C_{10}H_{16}$, 10–28%), α-terpinene ($C_{10}H_{16}$, 5–13%). and 1,8-cineole ($C_{10}H_{18}O$, 0–15%). The oil of *M. alternifolia* is volatile, with a flash point of 64 °C and vapor pressure of 15.7 Torr, which allows the monomer vapors to be produced under rotary vacuum and room temperature conditions. This makes the oil and its constituents highly suited to vapor-based deposition methods [15–17].

### 2.2. Graphene-organic device fabrication

Different graphene/organic semiconductor structures were fabricated to understand the interface charge accumulation/transport properties of graphene. Layers of $C_{60}$, pentacene, α–NPD, Alq3, and Al and Ag electrode were deposited onto the graphene layer using vacuum evaporation technique, at a pressure of $10^{-5}$ Torr and deposition rate of around 1 nm/min.

### 2.3. Current–Voltage measurement

The current–voltage (*I–V*) measurement was carried out using Keithley 2400 source meter. DC ramp voltage was applied to the graphene electrode with reference to the grounded Al/Ag electrode. The voltage sweeping rate was approximately 0.1 V/s.

### 2.4. Electric field induced optical second harmonic generation (EFISHG) measurement

The EFISHG measurement was performed to directly probe carrier processes in multilayer devices. EFISHG is material-dependent and hence the SHG will depend on the interface material and the wavelength of the laser used. EFISHG has been used extensively to selectively probe electrostatic field in a single layer within multilayer devices [18,19]. In the graphene/pentacene/$C_{60}$/Al device, injected charges $Q_s$ accumulate at the pentacene/$C_{60}$ interface. Consequently, under DC voltage application, electrostatic field in the $C_{60}$ layer ($E_2$) is given as

$$E_2 = \frac{1}{d_2}\frac{C_1}{C_1 + C_2}V + \frac{1}{d_2}\frac{Q_s}{C_1 + C_2} \quad (1)$$

where $d_2$ is the $C_{60}$ layer thickness, $C_1$(=1.2 nF) and $C_2$(=1.8 nF) are capacitance of pentacene and $C_{60}$ layers, respectively, as an equivalent circuit element in the terms of the Maxwell-Wagner effect model [20]. Here, we define the positive electric field as one that points from the graphene to Al electrode in the layers. The SHG light is emitted from the $C_{60}$ layer with the laser pulse irradiation (laser wavelength: 1000 nm [18]). The intensity of the SHG light is proportional to the square of $E_0$ (=$E_2$) as

$$I_{2\omega}\alpha|E_0|^2 \quad (2)$$

The electric field in the pentacene layer (thickness, $d_1$) is obtained by using the relationship

$$V = E_1 d_1 + E_2 d_2 \quad (3)$$

Consequently we can analyze carrier processes $Q_s$ (=$\varepsilon_2 E_2 - \varepsilon_1 E_1$ where $\varepsilon_1$ and $\varepsilon_2$ are dielectric constant of pentacene and $C_{60}$, respectively) based on Eqs. (1)–(3). Noteworthy that using double-layer structure device is very helpful to discuss the space charge field effect (2nd term of eq. (1)) due to accumulated charge $Q_s$ and the polarity of transport carriers.

### 2.5. Charge modulation spectroscopy

Charge modulation spectroscopy (CMS) was carried out using experimental procedures described in our previous study [21]. White light from a halogen lamp was used as a probing light. Briefly, the light was focused on samples with a spot size of 10 μm from silica/graphene side. The reflected signal was analyzed by a spectrometer and a high sensitivity cooled charge coupled device (CCD) image sensor. DC voltages were applied to graphene devices, by using Keithley 2400 source meter. CMS records a modulation spectrum $(R_1 - R_0)/R_0$ where $R_1$ is a reflectance spectrum with varied voltage $V$ in referenced to spectrum $R_0$ at a reference voltage $V_0$. In present CMS measurement, $V_0 = -10$ V was used. Figs. S1 and S2 show the experimental system we used for Electric Field Induced Second Harmonic Generation and Charge Modulation Spectroscopy.

## 3. Results and discussion

In order to develop graphene-based resistive devices, high-quality large-area graphene samples were produced from *Melaleuca alternifolia* essential oil following the procedure outlined in Ref. [14]. The oil-derived samples exhibited the signature Raman peaks of graphene. The vertical orientation and long reactive edge of large-area defect-free graphene sheets can be effectively utilized in many environmentally-sustainable electronics applications [22–24].