

Multilayer Graphene for Flexible Optoelectronic Devices [†]

Vera Marinova ^{1,2,*}, Stefan Petrov ², Blagovest Napoleonov ^{1,3},
Jordan Mickovski ³, Dimitrina Petrova ^{1,3}, Dimitre Dimitrov ^{1,4},
Ken Yuh Hsu ⁵ and Shiuan Huei Lin ²

¹ Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; blgv@abv.bg (B.N.); d_kerina@abv.bg (D.P.); dzdimitrov@issp.bas.bg (D.D.)

² Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan; st5pob@gmail.com (S.P.); lin@cc.nctu.edu.tw (S.H.L.)

³ Faculty of Engineering, South-West University “Neofit Rilski”, 2700 Blagoevgrad, Bulgaria; mickovski_j2@yahoo.com

⁴ Institute of Solid State Physics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

⁵ Department of Photonics, National Chiao Tung University, Hsinchu 30010, Taiwan; ken@cc.nctu.edu.tw

* Correspondence: vmarinova@iomt.bas.bg or veramarinova@nctu.edu.tw

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Abstract: Graphene has attracted considerable interest as a prospective material for future electronics and opto-electronics. Here, the synthesis process of large area few layers graphene by Atmospheric Pressure Chemical Vapour Deposition (APCVD) technique is demonstrated. Quality assessments of graphene are performed and confirmed by Raman analysis and optical spectroscopy. Next, graphene was transferred on Polyethylene Terephthalate (PET) substrates and implemented as transparent conductive electrode in flexible Polymer Dispersed Liquid Crystal (PDLC) devices. The stability of the sheet resistance after 1200 bending tests of graphene/PET structure is demonstrated. Their electro-optical properties, such as voltage-dependent transmittance and flexibility behavior are measured and discussed. The obtained results open a great potential of graphene integration into the next generation Indium Tin Oxide (ITO) free flexible and stretchable optoelectronics.

Keywords: graphene; CVD synthesis; sheet resistance; bending test; PDLC devices

1. Introduction

Graphene, an atomically thin two-dimensional material, is already proved to be very potential material for versatile applications in different areas of science and modern technologies. The enormous interest is motivated by the graphene's distinctive properties as excellent optical transparency, ultra-high carrier mobility, elasticity, high mechanical strength, thermal and chemical stability, etc. which are successfully utilized in flexible and bendable optoelectronics, energy harvesting structures, biomedical sensors [1–3]. Moreover, graphene is regarded as the perfect optically transparent conductor to replace the currently widely used ITO [1]. Furthermore, graphene enables fabrication of curved surfaces and transformed shapes and shows high potential in flexible displays, foldable touch screens, paper-like displays, curved and flexible solid-state lighting devices and so on [4–7].

Among the extensively used methods to synthesize graphene as mechanical exfoliation, liquid-phase exfoliation, chemical synthesis, epitaxial growth on silicon carbide, Chemical Vapor

Deposition (CVD) technique becomes the most popular and promising way for scalable graphene production [8–14]. Recent advances of CVD growth on metal substrates (Cu, Ni, Pt, Pd, Ir, Fe) led to the availability of large-scale and high-quality graphene, with controllable number of layers, limited defects and shows the best performance of graphene as transparent conductive films.

Typically, CVD processes involve two steps: the activation of gaseous reactants and a chemical reaction to form a stable solid deposit over the metal substrate. Generally, CVD can be divided into two types of process: (I) thermal assisted CVD and (II) plasma-enhanced CVD. The thermal CVD itself can be realized under low pressure (LPCVD) method or atmospheric pressure (APCVD) method commonly used for production of single, bi-layer or multilayer graphene. Although CVD growth of single layer graphene, due to its superior electrical transport properties, is highly anticipated despite being real challenging, the importance of multilayer graphene has rapidly grown because of its unique advantages for flexible optoelectronics providing ultra-flexible and transparent electrical contacts [11–17]. In this aspect synthesis of multilayer graphene is important issue; moreover it can provide superior electrical properties with the minor trade-off with optical transmittance reduction. For example, the roll to roll large area production [18] makes graphene a realistic candidate to be used in mass-produced flexible optoelectronic devices, organic and solid state solar cells, super capacitors, etc.

Recently, Polymer-Dispersed Liquid Crystals devices become very attractive for applications as outdoor displays, switchable privacy glasses, energy saving windows, light shutters, projection displays and so on [19,20]. In principle, PDLC are composite mixture of liquid crystal (LC) molecules randomly dispersed in a solid polymer matrix and due to the refractive index mismatch between the polymer matrix and the LC molecules. PDLC are naturally opaque (scatter the light at the initial state). PDLC can be switched from the light-scattering to the transparent state by application of an external electric field, which support the refractive indices match between the LC molecules and the polymer, and this functionality determines the unique behavior of PDLC devices.

In this study, the optical and electrical properties of multilayer graphene grown by APCVD were determined and the application of graphene films as transparent electrodes in flexible PDLC devices have been addressed.

2. Experimental

In this work, graphene was synthesized by APCVD method using copper foil (Alfa Aesar 99.8% purity, 25 μm thickness) in a set-up shown at Figure 1a. A preliminary surface cleaning of the Cu foil was performed by sonication in acetone and propanol followed by deionized (DI) water rinsing and dry blowing with nitrogen. Before loading into the CVD tube reactor the Cu foil was treated with acetic acid to remove the superficial copper oxide. First, the Cu foil was annealed at 1030 $^{\circ}\text{C}$ for 30 min in argon (Ar) and hydrogen (H_2) atmosphere. After that, CH_4 gas flow was introduced and the growing process continue in the gas mixture ratio of $\text{Ar}:\text{H}_2:\text{CH}_4 = 450:50:10 \text{ cm}^3/\text{min}$. The CH_4 served as a carbon feedstock gas and was used only during the growth process. Finally, when the growth process completed the reactor tube was rapidly cooled to room temperature with a speed of 50 $^{\circ}\text{C}/\text{min}$ (Figure 1 b). By following the above procedure continuous large area of graphene on Cu foil surface was synthesized.

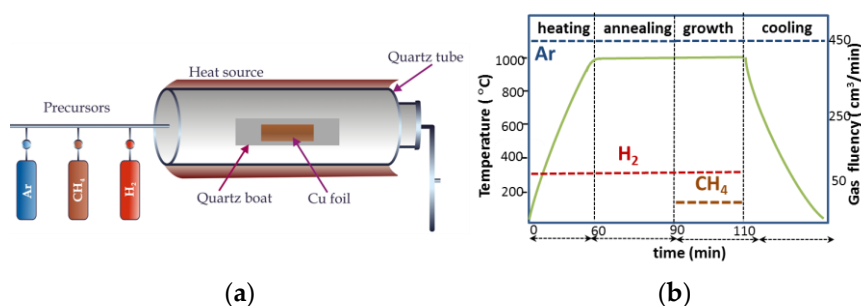


Figure 1. (a) APCVD experimental set-up and (b) temperature/time diagram of growing multilayer graphene.

The graphene film was transferred on 100 micrometer thick PET substrates by spin coating a poly(methyl-methacrylate) PMMA (4% in anisole) on the top of graphene/Cu sheets. The PMMA/graphene/Cu foil was floated on $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution to etch the Cu foil. The resultant film with PMMA and graphene was transferred to PET substrates, followed by removal of the PMMA by using substrates heating in acetone at 80 °C.

Raman spectroscopy was used to analyze the quality of the graphene layers and confirming multi-layer graphene structure. The Raman equipment consists of a 488 nm DPSS laser, spectrometer (HORIBA, Lab RAM HR) and CCD. An objective lens (100X, N.A = 0.9) was used to focus the laser with a resolution of $\sim 1 \mu\text{m}$ at the laser intensity at 10 mW.

The optical transmittance spectrum of graphene/PET was measured at room temperature using an Ultraviolet-Visible-Near-infrared (UV-VIS-NIR) spectrophotometer Shimadzu UV-3600. The same measurement was performed on PET substrate for comparison.

The sheet resistance was measured using a four-point probe technique on an Ossila apparatus. Computerized home-built bending setup with an ESP301 control platform to stimulate bending at different radius was used for bending test of the graphene/PET samples. The sheet resistance of the samples was measured in the interval up to 1200 bending cycles.

Based on the above characteristics, several graphene/PET substrates have been selected for PDLC devices fabrication. First, empty cells were assembled by composing graphene/PET substrates facing the graphene layer each to other, separated with Mylar spacer (12 μm) in order to keep the uniform thickness. Then, PDLC mixture was made using UV-curable monomer NOA65 and E7 nematic liquid crystal at 30 : 70 wt.% ratio. Next, the LC/monomer mixture was injected into an empty cell and exposed with ultraviolet light ($\lambda = 365 \text{ nm}$) for 15 min to polymerize NOA65. As a result of a phase separation, formation of randomly dispersed LC droplets in a polymer matrix appears.

The electro-optical characteristics of graphene/PET supported PDLC devices were measured by using a He-Ne laser as light source and applied alternating current (AC) voltage at 1-kHz frequency.

3. Results and Discussions

Figure 2a shows the Raman spectrum of graphene grown on Cu foil, characterized with very strong G-peak, located at $\sim 1582 \text{ cm}^{-1}$ and 2D-peak, located at $\sim 2718 \text{ cm}^{-1}$ with an intensity ratio $I(2D)/I(G)$ of ~ 0.474 . The D-peak (located at 1350 cm^{-1}), which is a result of the defects and inhomogeneity in the sample, has moderate intensity, indicating the formation of good quality multilayer (4 to 5 layers) graphene [21].

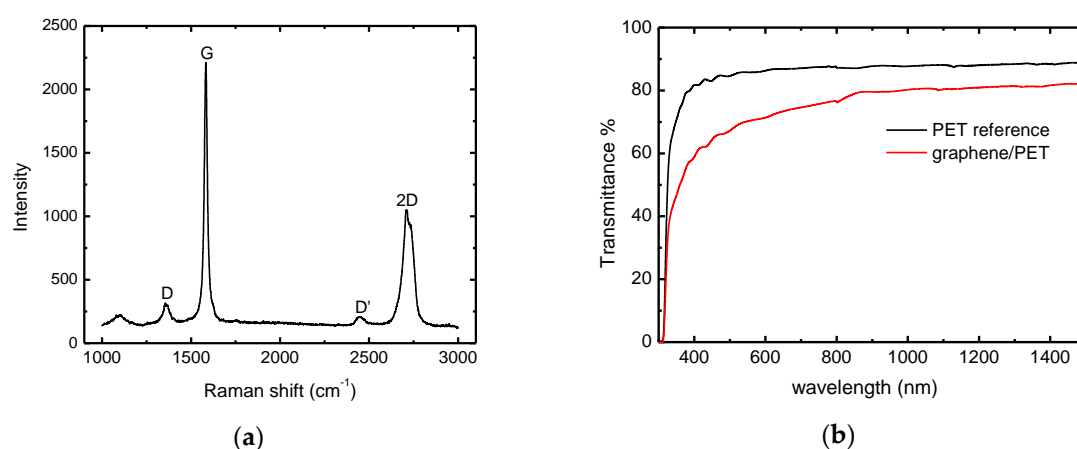


Figure 2. (a) Raman spectrum of graphene grown on Cu foil and (b) Optical transmittance spectra of graphene/PET.

The optical transmittance spectrum of graphene/PET at visible and near infrared spectral range is shown at Figure 2b. A comparison with the transmittance of blank PET is also presented for reference.

The sheet resistance dependence on the number of bending cycles was tested by using home-built bending setup shown at Figure 3. Multilayer graphene demonstrates excellent bending ability for more than 1200 times of cycling as shown in Figure 3c. Hence, by controlling the number of graphene layers, optical and electrical properties can meet the up-to-date standard requirements for ITO-free optoelectronics with acceptable sheet resistance and optical transparency values [22].

The remarkable sheet resistance stability under bending of graphene opens many opportunities for applications in flexible, stretchable and bendable optoelectronics.

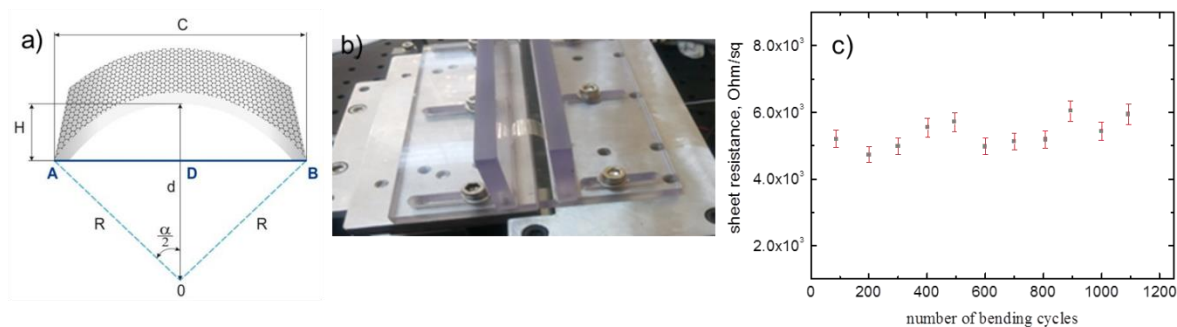


Figure 3. (a) Schematic diagram for bending radius (R) calculation, (b) part of bending test set-up and (c) sheet resistance dependence of the number of bending cycles at 2.5 mm bending radius.

Based on the above performed characteristics, an application of multilayer graphene on PET as transparent conductive layer in flexible PDLC devices is demonstrated.

Figure 4a shows the schematic structure of PDLC device using the graphene films as electrodes. The transmittance behavior was monitored as a function of applied voltage and it is shown at Figure 4b. We measured the threshold voltage V_{th} (defined as an applied voltage value to reach 10% of the maximum transmittance T_{10}) for turning on the PDLC device of ~ 20 V and saturation voltage V_{sat} (defined as a value of applied voltage to reach 90% of maximum transmittance T) of ~ 70 V. As a result, by the application of an appropriate electric field the intensity of the transmitted light throughout the structure can be controlled.

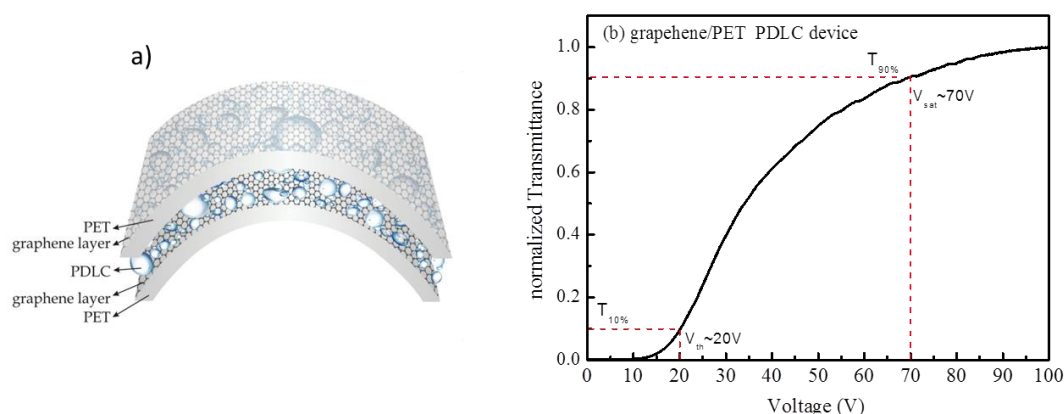


Figure 4. (a) Schematic structure of PDLC flexible device (b) Voltage-transmittance characteristics demonstrating “on” and “off” states of the device.

4. Conclusions

This work demonstrates growth, characterizations and applications of multilayer graphene as transparent conductive electrode for flexible display devices. Multilayer graphene was synthesized

by Chemical Vapor Deposition technique and its optical and electro-optic characteristics were measured. Multilayer graphene on a flexible PET substrate demonstrates excellent bending ability with almost constant sheet resistance values over 1200 times of bending. The demonstration of flexible PDLC device opens a great potential of graphene integration into the next generation flexible and stretchable ITO-free optoelectronics.

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