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Development of a multi-steps CVD process to produce bi-layers graphene for anode of Organic Light Emitting Diodes**P. Trinsoutrot¹, M. Brignone², H. Vergnes¹, B. Caussat¹, D. Pullini²**¹Université de Toulouse, Laboratoire de Génie Chimique, ENSIACET/INP Toulouse
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Graphene is one of the most interesting candidates for the next generation of transparent conductive electrodes (TCEs) for electrical devices, because of its unique electronic structure. Furthermore, the optical transparency of graphene films surpasses that of conventional TCEs such as indium tin oxide (ITO) [1]. However, graphene anode for Organic Light Emitting Diodes (OLEDs) still presents several problems owing to its low work function and high sheet resistance [1], which may be related to a poor control of graphene quality.

Chemical vapor deposition (CVD) on copper from methane seems to be the most efficient approach to form high quality transferable graphene for opto-electronic applications, due to the potential for commercially viable production at large scale. However, CVD processes need to be optimized for obtaining selective single or bilayers growth, as well as highly crystalline, full coverage, large area domains [2]. Indeed, CVD graphene films are typically composed of relatively small polycrystalline flakes. A high density of grain boundaries degrades the properties of graphene [2]. Thus, it is desirable to prepare large single-crystal graphene to minimize the impact of defects existing at grain boundaries. The most recent studies of the literature show that this objective can be met by using very low concentration of methane (<100 ppm), but in these conditions, it is difficult to obtain a full coverage of the substrate [3]. The most efficient way to obtain a continuous high quality monolayer of graphene seems to use a multi-steps process, first involving a very low methane concentration in order to form strictly monolayer graphene flakes with low nucleation density. Then, methane concentration is progressively increased, to counterbalance the decrease of the active catalytic copper surface [3].

In the present study, a two-step process then a three-steps one have been developed only differing by the third step, in order to produce graphene for OLED application. Methane diluted into hydrogen and argon was used on copper foils (25 μm thick, 99,999% Alfa Aesar) of 2x2 cm^2 . The operating temperature was fixed at 1,000°C and the total pressure was of 700 Torr. The hydrogen on methane inlet molar ratio was fixed to 800 for steps 1 and 2. The CH_4 concentration was of 10 ppm for step 1 and 40 ppm for step 2, and their duration was of 60 min for each one. For step 3, only 5 min long, the CH_4 concentration was of 9,000 ppm and the H_2/CH_4 ratio of 10. Optical microscope and Raman spectroscopy measurements (confocal Raman microscope Labram – Horiba Yvon Jobin) were carried out to investigate the quality and extend of graphene sheets.

After the two first steps, graphene was strictly monolayer (2D (~2,670 cm^{-1})/G (~1,582 cm^{-1}) peaks average ratio equal to 7), with no disorder-induced D-peak (~1,350 cm^{-1}), but it was formed of discontinuous flakes of several tens of microns. This is why a third step was added. Optical micrographies indicated that graphene fully covers the Cu substrate after step 3. Raman spectra taken on different points of the three-steps sample are given in Fig. 1a. The 2D/G peaks average ratio is of 1.4, corresponding to bi-layers graphene. The average D/G ratio is of 0.06, showing excellent graphene crystalline quality. So, it appears that for these conditions, a quite high CH_4 concentration is necessary for the third step, to counterbalance the decrease of the active copper surface, thus maintaining a steady-state carbon ad-atoms supply to get full graphene coverage.

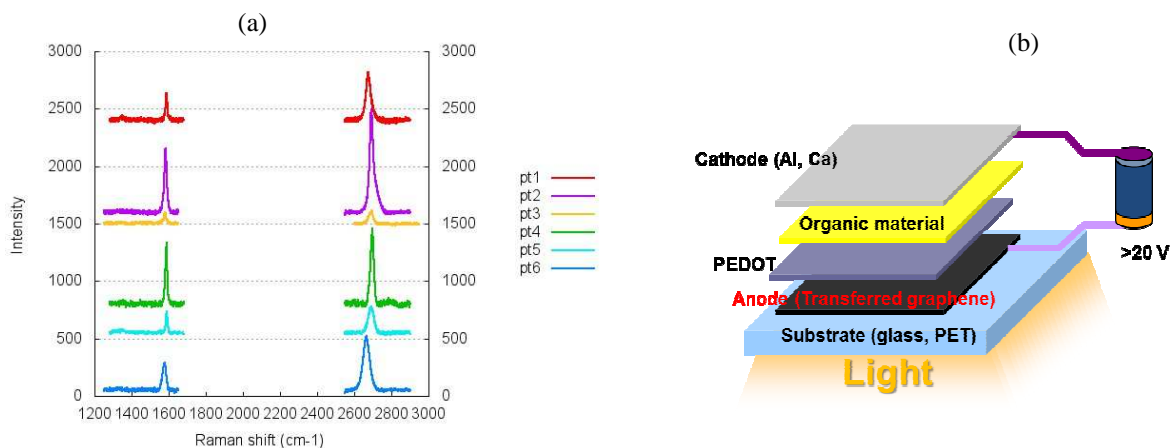


Figure 1: (a) Raman spectra after step 3 – (b) Schematic representation of a graphene OLED

The three-steps sample has been used for OLED fabrication. After transferring graphene on glass, a hole transporting layer, a water mixture of [poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)] PEDOT:PPS, was dissolved in 25%w isopropanol and deposited on the graphene surface by spin coating and dried at 50°C for 10 min (thickness \approx 50 nm), as shown in Fig. 1b. The quantity of isopropanol used is significantly larger than that used in the standard ITO-OLED to allow the colloid to properly wet the hydrophobic surface of graphene. A light emitting polymer (Merck PDY 132) was then deposited by spin coating at 1,800 rpm (thickness \approx 100 nm). The cathode, made of three metal layers (CA, Al, Ag, total thickness \approx 300 nm) was evaporated in vacuum chamber. The device was packaged with an epoxy resin layer and a thin glass substrate. The prototype fabricated in this way lighted up as shown in Fig. 2. The figure shows a first example of OLED working device made from said emitting polymer. As a matter of fact, an outline for the future is to improve the graphene transferring process on such hydrophobic surface in order to limit the presence of corrugations and wrinkles. Indeed, they could have created a thickness inhomogeneity of each layer of the emitting sandwich, which most likely is the main reason for the limited lighting area in this experiment.

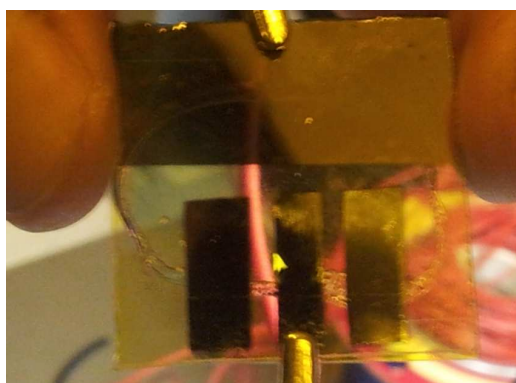


Figure 2: The graphene based OLED prototype

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