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Marker-free on-the-fly fabrication of graphene devices based on fluorescence quenching

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Abstract
Graphene has been dominating the electronic research community recently, with a brisk surge in proposals for its use in novel devices. The aspirations of 2D-carbon-based electronics largely rely on the availability of a mass-production technique to obtain wafer-scale graphene circuits. In this paper, we take a first step towards fulfilling this aspiration by demonstrating a rapid prototyping route for graphene-based devices. The method is based on our observation that graphene quenches the fluorescence from dyes. Utilizing this property, we use a confocal microscope to identify graphene flakes and perform the required lithography steps, bypassing the need for markers and other infrastructure such as atomic force microscopy or e-beam lithography. The versatility of this technique enables it to harbour ambitions of an automated process for large scale *in situ* assembly of graphene-based circuits.

S Supplementary data are available from stacks.iop.org/Nano/21/015303/mmedia

1. Introduction

Carbon-based devices are emerging to be primary candidates for a number of applications in a broad range of fields [1]. Among such candidates, semiconducting carbon nanotubes have been dominating the scene for more than a decade with their promise for high field-effect mobility and near-optimal device characteristics [2]. More recently, the two-dimensional form of carbon—graphene, which exhibits ballistic electronic transport and high crystalline quality at a sub-micron scale [3, 4]—has been generating widespread enthusiasm in many research fields. A range of applications are being envisioned for such sheets of semi-metallic carbon, including gas sensors [5], spintronic devices [6–8], terahertz oscillators [9] and the possibility to pattern complete electronic circuits on a single sheet [10]. The band structure of this exciting material can be tuned by controlling the width of the transport channels down to quantum-wire-like configurations, enabling transistor operation in such devices [11].

In order for graphene to be deployed in a widespread manner and to actuate its transition from potentiality to application, it is important to realize the capability of large scale production of graphene devices. Until now, e-beam lithography (EBL) has been the only method used for the fabrication of prototype graphene devices. However, since EBL is not easily scalable, graphene devices, like many other nanoscale devices, suffer from the inability to be easily deployed in marketable applications. Current methods require the identification of graphene with the help of markers on a substrate, followed by subsequent deposition of electrodes, thereby requiring at least two steps of EBL, one of which involves a manual alignment procedure. The identification is performed using an optical microscope and a specified oxide thickness is necessary for obtaining optimal contrast [12]. Here we propose a novel strategy involving just a single process step, without the use of markers. The graphene flakes are identified and the devices are fabricated on-the-fly using a confocal laser scanning microscope. The versatility of this technique

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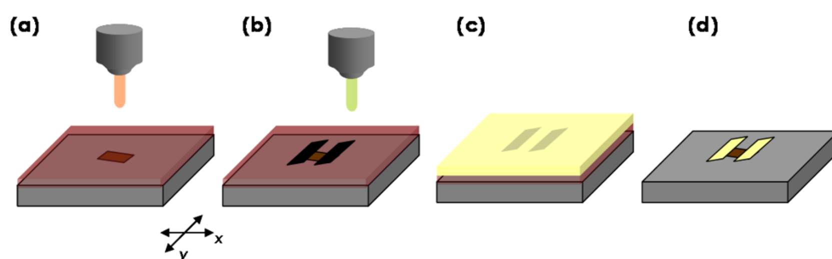

Figure 1. On-the-fly fabrication of a graphene device (schematic): (a) locating graphene using an *imaging laser* after the substrate is spin-coated with photoresist. (b) Drawing the required layout using a *write laser*; in this case windows for two contacts. (c) Evaporating the desired metal (Ti/Au) on the substrate and (d) final graphene device after lift-off/removal of resist.

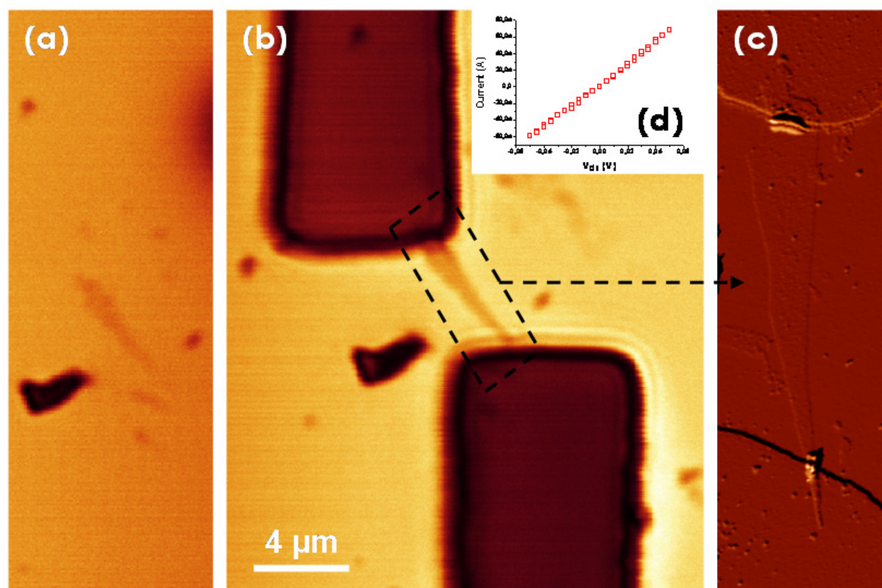

Figure 2. On-the-fly fabrication of a graphene device (experiment): (a) confocal image of a sample region recorded using the *imaging laser*, where the flake is identified, (b) confocal image of the same area after drawing the desired layout using the *write laser* followed by developing, (c) AFM image of the final device after metal deposition and lift-off and (d) I–V curve of the final device. Scale: x axis: bias voltage +/− 50 mV, y axis: current +/− 60 nA.

shows promise for the automated fabrication of graphene devices over a complete wafer with important consequences for applications.

2. Experimental details

Methods for obtaining graphene can be classified under physical and chemical techniques. Physical methods include micromechanical cleavage (exfoliation) of highly ordered pyrolytic graphite (HOPG) crystals [3] and epitaxial growth on silicon carbide [13, 14]. Popular chemical methods involve the reduction of graphene oxide originating from graphitic particles [15, 16]. While chemical methods show great promise for obtaining graphene flakes with high throughput, the high resistance of such flakes is still a matter of concern. In this work, the graphene flakes were prepared by exfoliation of HOPG and were then transferred onto a silicon wafer (highly p-doped) with a thermally grown 300 nm SiO_2 serving as the insulating gate dielectric. It has been shown that similar transfers can also be done to sheets grown from silicon carbide [17] and chemically derived graphene sheets [16]. Hence, the procedure outlined here can also be deployed for other sources of transferred graphene sheets.

Figure 1 shows a schematic describing the steps involved in our fabrication process starting from an exfoliated graphene sheet on the Si/SiO_2 substrate. The substrate is spin-coated with a photoresist (ma-P1215, micro-resist technology GmbH) and baked to obtain a 1.5 μm thick layer. ma-P1215 is a g- or i-line photoresist [18] with absorption maxima close to 436 or 365 nm. Illumination by UV light induces chemical changes in the resist, increasing the solubility of the exposed areas [19], which can be preferentially stripped off by dissolution in an appropriate developer solution (ma-D331, micro-resist GmbH). A subsequent metal evaporation step and a lift-off procedure finalize the device fabrication, providing metal regions only in the exposed areas. Usually, a mask is used to specify the layout of the electrodes. Although ma-P1215 is designed for UV exposure, we have observed that the coated resist still possesses a sizeable molar absorption coefficient up to visible wavelengths of around 580 nm. Chemical modifications can still be induced by irradiating with low energy laser sources. We utilize this property to devise

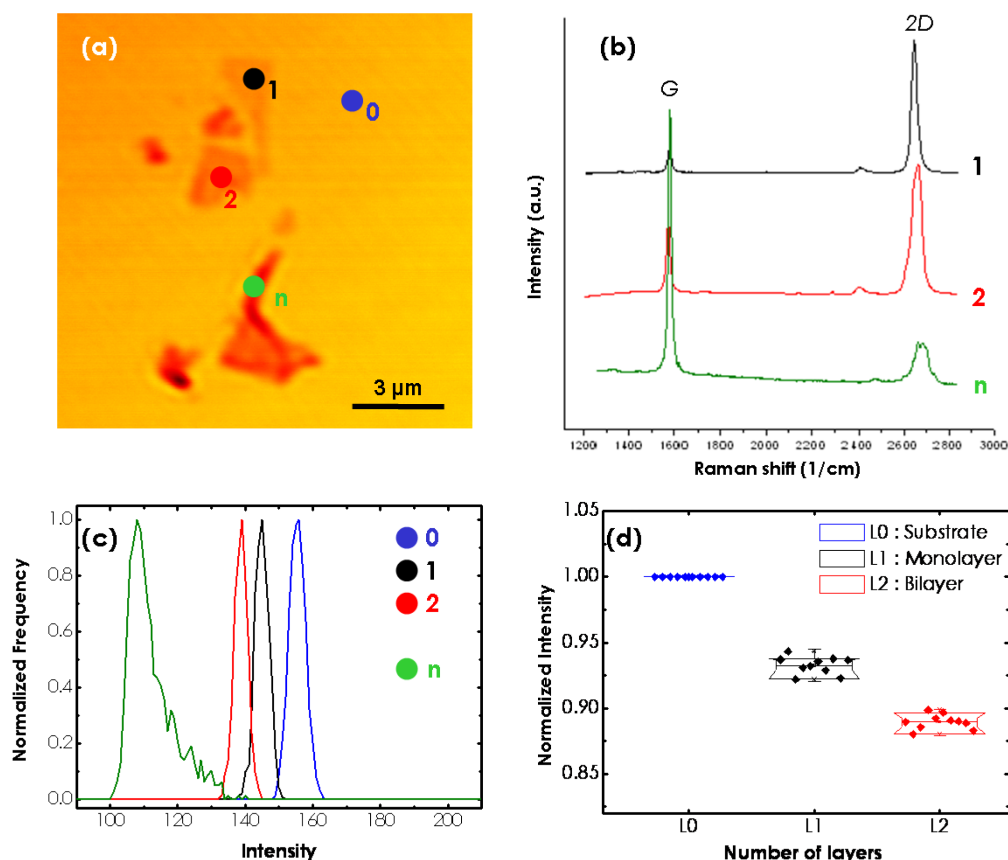

Figure 3. (a) Confocal images of a sample region showing a distribution of flakes with differing layers: **1** is a monolayer, **2** is a bilayer, **n** is a multilayer and **0** represents the substrate, (b) Raman spectra of the corresponding flakes, (c) histogram of the fluorescence intensities of the selected regions, showing that the recorded intensity is inversely proportional to the number of layers and (d) a plot of the normalized intensities versus the number of layers, which can be used as a calibration scale to determine the number of layers in an unknown sample. In addition to the data points from (c), this plot contains data points from other flakes on other samples.

a fabrication protocol, wherein the exposure is performed at a wavelength of 476 nm (*write laser*) instead of UV light. Another important observation we have made is that the fluorescence from the photoresist is considerably quenched by the underlying graphene flakes, as discussed in detail later. This enables the imaging of graphene flakes without the need for an external optical microscope. We use a wavelength of 633 nm (*imaging laser*) to locate and identify the graphene flakes (as depicted in figure 1(a)), since the photoresist does not undergo significant chemical changes upon illumination at this wavelength. After the flake is identified, the *write laser* is utilized to perform the exposure. The desired layout is obtained by scanning the piezostage using a computer-controlled interface (see figure 1(b)), avoiding the need for a separate mask. After a development step the desired metal is evaporated onto the sample (figure 1(c)). The procedure is completed (figure 1(d)) by removing the residual photoresist by means of a lift-off procedure in 1-methyl-2-pyrrolidone (55 °C for 3 h), thus yielding a contacted graphene device.

Figure 2 shows a representative sample that was prepared using the fabrication procedure described above. Figure 2(a) shows a confocal image (recorded using the *imaging laser*) of the sample after deposition of the photoresist, where the graphene flake to be contacted is identified. After imprinting the desired structure using the *write laser*, the sample is developed in an ma-D331 solution. The etched areas are distinctly seen in figure 2(b). Figure 2(c) displays an atomic force microscope (AFM) image, while figure 2(d) shows the transport characteristics of the final graphene device after the deposition of metal (1 nm Ti/10 nm Au) followed by lift-off. The gap between the electrodes is around 4 μm, which can be adjusted according to the required transport channel. In other samples (such as the one in figure S2—supplementary information available at stacks.iop.org/Nano/21/015303/mmedia), we have obtained gap sizes down to around 2.5 μm, suggesting a resolution limit of around 5λ to 6λ. Although this would suffice for a number of common applications, some of the more exciting applications may require sub-micron gaps between electrodes. This can be obtained by optimizing the fabrication procedure and by using an appropriate high resolution photoresist [18]. In addition, the chemical structure of the resist can be optimized for the wavelength of the *write laser*. Alternative scanning techniques such as near-field microscopy may be evaluated for obtaining a resolution below the diffraction limit as low as 50 nm [20]. However such a technique is prone to other limitations such as very low speed.

While we have demonstrated that we can fabricate devices in one step using just the confocal microscope and without the employment of markers, there is another important concern.

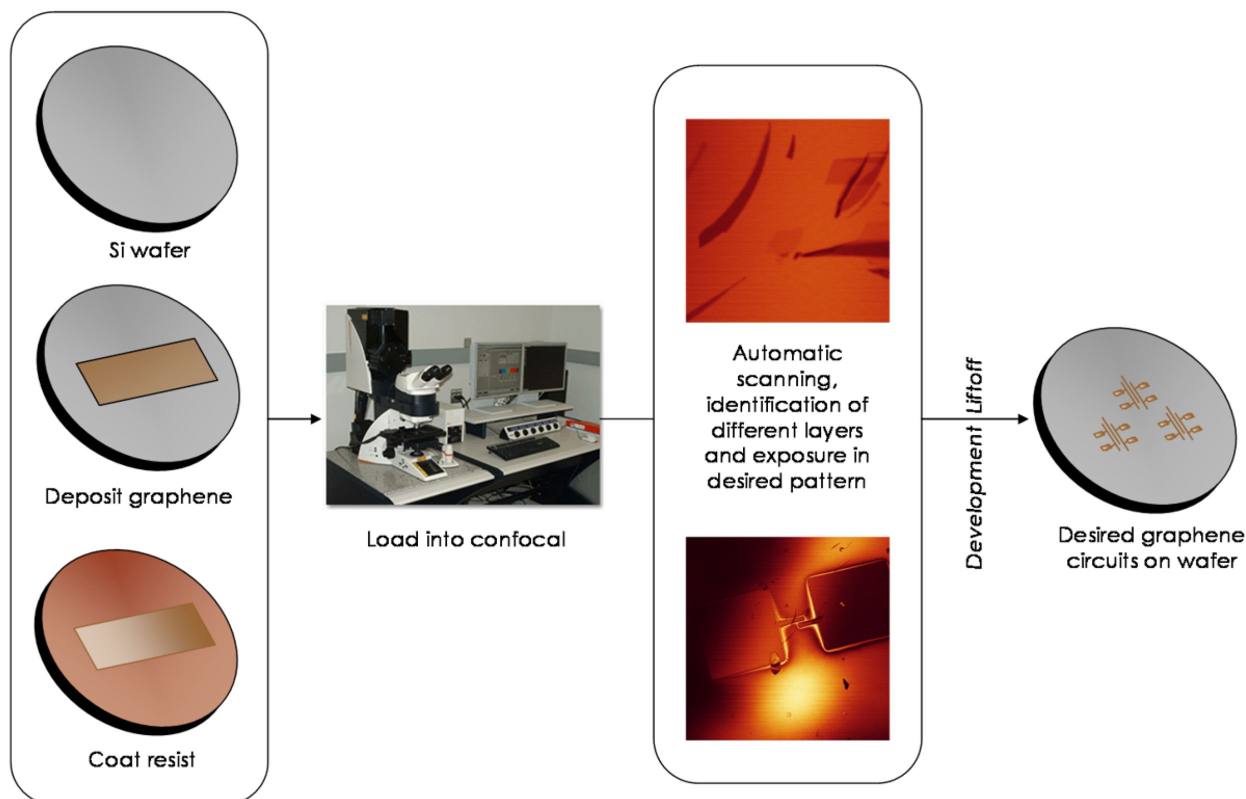

Figure 4. Rapid prototyping of graphene devices on a wafer (schematic): in the first step, graphene flakes are deposited on a large wafer and coated with a photoresist, after which it is loaded into the confocal microscope. A computerized scanning stage is used to scan the whole wafer or regions of the wafer using the *imaging laser*. The desired flakes and the number of layers are identified using image processing algorithms and calibration plots (such as the one in figure 3(d)). A standard or user-specified layout is subsequently imprinted in the regions of interest using the *write laser*. The wafer is then removed from the microscope, developed, metal evaporated and the resist lifted off to obtain a multitude of graphene devices on the wafer in a relatively short period of time.

Almost all of the graphene preparation methods reported until now deliver a distribution of sheets with varying numbers of layers. Hence, before contacting it is important to identify the number of layers in the graphene flake of interest. While AFM is helpful to a certain extent in estimating the height, it is difficult to assert the number of layers using this technique due to the influence of substrate inhomogeneities and adsorbates [21]. A more reliable technique is local Raman spectroscopy, which has been successfully used to unambiguously estimate the number of layers. The shape and distribution of the sub-peaks in the Raman 2D band and the position of the Raman G-band are used for performing this analysis [22].

Raman spectroscopy can be used in our scenario to estimate the number of layers by attaching a spectrograph to the output port of the confocal microscope. However, this requires expensive equipment and the recording of a Raman spectrum is a time-consuming step. Here, we propose an alternative simple method for identification that does not require any additional equipment. This method is based on our observation that the fluorescence from the photoresist is quenched in the presence of graphene [23], analogous to observations made on carbon nanotubes [24]. This is already apparent in the confocal images shown in figure 2, where the flake appears darker with respect to the background. The extent of fluorescence quenching is found to be proportional to the number of layers in the graphene flake. This is clear from the confocal image shown in figure 3(a), where it can be seen that the recorded fluorescence intensity is lower on the flakes with respect to the background. Three regions of interest have been identified as monolayer, bilayer and multilayer flakes with the help of Raman spectra recorded independently (figure 3(b)). Figure 3(c) shows a histogram of the fluorescence intensities from the three regions in addition to the background intensity. It can be seen that the intensity is maximum on the substrate and goes down sequentially for single, bi-and multilayers. Based on this a normalized calibration plot can be derived as shown in figure 3(d), which can be used to determine the number of layers in an unknown flake.

3. Conclusions

Based on the foregoing discussions and the presented results, we propose a strategy for the rapid prototyping of graphene devices on a wafer scale. This is summarized in figure 4, where we start with a Si/SiO_2 wafer containing graphene flakes obtained by any production method of choice. Following this, the wafer is coated with a photoresist and loaded into the confocal microscope. The whole wafer or a sub-region is then scanned using the *imaging laser* (633 nm) and graphene flakes

identified by image segmentation techniques [25]. With the help of calibration plots as shown in figure 3(d), the number of layers in every flake is estimated. The identification of the flakes and the estimation of the number of layers can be easily automated with standard image processing algorithms [26]. At this stage, a standard or a user-specified layout can be produced by using the *write laser* (476 nm). Subsequently, the exposed wafer is developed, metal is evaporated and the resist lifted-off to obtain the final wafer with the desired devices or circuits with minimal user intervention. As is apparent, the whole procedure can be carried out in a closed sequence. In comparison to today's procedures, which require elaborate search, alignment and verification of the number of layers, our technique is estimated to provide a considerable improvement in fabrication speed (see table S1 in supplementary information available at stacks.iop.org/Nano/21/015303/mmedia).

On the other hand, it is important to be mindful of the limitations of our technique. There are two aspects of the large scale fabrication of graphene devices. The first step is to obtain uniformly distributed sheets and the second one concerns the rapid processing of individual flakes. While our proposed method addresses the latter aspect, its success relies on the availability of a good density of flakes on the substrate. Moreover, in contrast to photolithography, our on-the-fly lithography is a serial procedure. As a result, the throughput is limited by the scanning speed and the imaging resolution. In spite of these limitations, the fewer number of steps required, the absence of the need for markers and the use of just one instrument makes it a suitable tool for rapid prototyping in comparison to currently prevalent methods such as EBL (see table S1 in supplementary information available at stacks.iop.org/Nano/21/015303/mmedia).

In summary, we have devised a new method for on-the-fly marker-free fabrication of graphene devices using a single instrument. The method is based on the fact that graphene quenches the fluorescence of dyes. The quenching of fluorescence is found to be proportional to the number of layers in the flake. This rapid prototyping technique shows promise for the possibility to realize wafer-scale graphene-based circuits and devices in a comparatively short timescale. This technique will be exceptionally practical to the research community in the wake of continual investigations that single-layer, bilayer [27] and few-layer graphene [28] are currently being subjected to in laboratories around the world. From an application perspective, such a possibility to promptly realize wafer-scale circuits will accelerate the entry of graphene-based devices into real-life applications.

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