Graphene patterning by nanosecond laser ablation: The effect of the substrate interaction with graphene

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Abstract. This paper focuses on the development of patterned graphene/substrate by means of green nanosecond pulse laser irradiation. Monolayer graphene samples supported on a Si/SiO₂ substrate were patterned using 532 nm laser irradiation under fluence conditions ranging from 31 mJ/cm² and to 4240 mJ/cm². Raman spectroscopy was used to investigate the effect of laser irradiation on the graphene. It was found that at 356 mJ/cm² selective ablation of the graphene occurs. However, at fluence values above 1030 mJ/cm² (when damage to the substrate is observed) no ablation of the graphene takes place. In contrast, its graphenic structure was found to have been modified. Only at fluence values where the ablation of the substrate occurs, is graphene eliminated in an area almost equivalent to that of the ablated substrate. In this case, additional damage to the graphene sheet edges is produced. The increment in the number of oxygenated functional groups in these regions, as measured by XPS spectroscopy, suggests that this damage is probably caused by thermal phenomena during the ablation of the substrate.

Keywords: CVD Graphene, laser scribing, nanosecond laser, pulsed laser

1. Introduction

Graphene has emerged in recent years as a highly attractive material because of its outstanding properties [1][2]. In particular, graphene possesses an excellent charge carrier mobility (up to 200000cm²V⁻¹s⁻¹ in suspended structures [3]) that makes it an ideal material for use in high frequency electronics. In addition, it shows exceptional mechanical flexibility when bent and/or stretched [4][5]. The combination of these two characteristics opens up a wide range of possibilities for the design and development of novel flexible electronic devices.

From an experimental point of view, the control of graphene properties for different applications and for the integration of the materials in the devices often requires the patterning of the material so that it conforms to specific dimensions and geometries [6]. This is the case of the preparation of transistors [7][8] or transparent electrodes [9][10]. In these cases, the selective removal of graphene by laser irradiation, which is a non-contact patterning technique, allows the complex patterning of graphene films to within a range of tens of micrometers [11] without the need for expensive and time consuming processes such as UV photolithography. This process allows the exploitation of graphene's exotic electronic properties for geometry-dependent applications and facilitates its integration of in microdevices.

Ultrafast pulse lasers, with a frequency pulse ranging from 10⁻¹² to 10⁻¹⁵ s, are the most widely used systems for patterning graphene for electronic devices. This is because, compared to the

removal of materials by conventional and lower-cost long-pulse laser treatment, these lasers minimize the diffusion of energy through the material, and therefore create smaller heat-affected zones [12][13]. Although femtosecond lasers have been widely used to enhance the resolution of the scribe lines [14][15][16][17][18][19], several studies have recently reported the patterning of graphene by means of nanosecond pulse lasers which offer a wider choice of wavelengths than femtosecond lasers. In addition, compared to femtosecond, nanosecond lasers constitute a reliable and robust technology that can be easily implemented on an industrial scale. Furthermore, nanosecond pulsed laser are widely used nowadays in the nanofabrication of multiple devices such as nanoparticle formation among others [20][21][22]. Mackenzie et al. demonstrated that a picosecond laser can be successfully used to ablate graphene without causing any damage to the silicon dioxide substrate [23]. Wakaya et al. reported the defect generation or ablation of few-layer graphene onto Si/SiO₂ substrates by means of a nanosecond 533 nm laser, demonstrating that the application of laser power densities of 1.4 MW/cm² increases the resistance of few-layer graphene, while laser power densities of 3.5 MW/cm² cause the complete removal of the graphene material, up to a threshold graphene thickness of 10 nm (the laser depth penetration into graphene) [24][25]. Kiisk et al. observed that the presence of impurities in the graphene sample and/or the lack of thermal contact between the graphene and substrate substantially modify the threshold energy density of the graphene under the same experimental conditions. They also suggested that, in the case of using a substrate with a threshold energy density in the range of that graphene, both processes might mutually influence each other, modifying the damage mechanisms in the graphene [26]. However, to date no information regarding this issue has been reported in literature.

Accordingly, this paper studies the effects of irradiation with a nanosecond laser on mono/bi layer graphene transferred to a Si/SiO₂ substrate by analyzing the Raman and XPS spectra of the imaged samples. To evaluate the influence of substrate damage on graphene ablation, energy densities in the range of the threshold energy density of the substrate were used.

2. Experimental

The single layer graphene used in this work was obtained by means of a CVD process described elsewhere [27]. Briefly, the process was carried out using a commercial device (EasyTube 3000, FirstNano) and a copper foil (AlfaAesar, 0.025mm thick, 99.8% purity) as catalyst substrate. The growth process consisted in a first step of annealing at 1000°C in a hydrogen atmosphere in order to prepare the catalyst, followed by a one-hour growth step during which methane and hydrogen were introduced at flow rates of 1:10 and at 1000°C. The graphene transfer was carried out by attaching a strip of polymer film to the upper surface of the graphene and then by chemically etching the copper foil. Once the metal foil had been totally removed, the graphene layer attached to the polymer was extracted from the chemical etching solution and placed onto Si/SiO₂ (silicon dioxide layer of 285nm) which had previously been treated with a piranha solution and washed with deionized water. Finally, the polymer was removed by immersing it in acetone. In this work, the polymer used was GelPak[®] (DGL-20-04, Gel-Pak, Delphon), the commercial etchant was APS-100-Transene and Si/SiO₂ wafers were purchased from University Wafer.

The graphene was irradiated using a Nd:YAG nanosecond laser (PowerLine E, Rofin), with a pulse duration of 20ns and a wavelength of 532nm. The laser intensity profile is Gaussian, with M² factor (beam quality factor) lower than 1.05. The laser was set to emit a laser spot 25 µm in diameter. The fluences used ranged from 31 mJ/cm² to 4240 mJ/cm². The laser beam was homogenized and shaped to a strip of ≈20 µm by moving the graphene sample during processing. The calculated degree of overlapping was of the order of 50%, resulting in a 2 beam irradiation at every point on the graphene sample.

Optical micrographs were obtained on a Zeiss axioplan operated in air. Raman spectra were recorded on a Jobin-Yvon T64000 spectrometer employing a subtractive triple configuration. The samples were analysed by backscattering z(xy)z geometry using the 5145 Å line of an Ar

laser. The high resolution XPS C1s spectra were obtained on a VG-Microtech Mutilab 3000 device. Curve fitting of the C1s spectra was performed by applying a Gaussian-Lorentzian peak shape technique and carrying out a Shirley background correction. The binding energy profiles were deconvoluted into the following categories: undamaged structures of Csp²-hybridized carbon (284.5 eV), damaged structures or sp³-hybridized carbons (285.5 eV), C-O groups (286.5 eV), C=O functional groups (287.7 eV) and COO groups at 288.7 eV).

3. Results and discussion

Prior to the transfer process, the Si/SiO₂ substrate was treated with a piranha solution in order to improve the adhesion of the graphene. A Raman analysis of the transferred graphene sample confirmed the presence of monolayers (figure 1) with the spectrum showing an intense G peak at 1580 cm⁻¹, a low intensity D-peak at 1350 cm⁻¹ corresponding to the presence of some defects (with an I(D)/I(G) close to 0.15) and a 2D peak at 2690 cm⁻² with almost twice the intensity of the D peak. This spectrum was obtained at almost all points of a 1cm² area of graphene and only a small number of islands of bilayer graphene were observed (10%). AFM measurements also confirmed the presence of monolayers with an average sheet height of 0.8-1nm²⁸, the range one would expect for single-layer graphene firmly attached to the substrate (see S.D.).

Figure 1: Raman spectra of the graphene transferred to the Si/SiO₂ substrate.

Figure 2 shows the optical images of the graphene/Si/SiO₂ samples after irradiation by the nanosecond pulse laser at frequencies leading to fluence values in the ≈ 31 to ≈ 4240 mJ/cm² range. The images evidence that, although only fluences above ≈ 2180 mJ/cm² resulted in the ablation of the substrate under the graphene, damage to the substrate appeared after irradiation at fluences higher than ≈ 1030 mJ/cm² (figure 2 d,e). Substrate damage is evident and easily distinguished from graphene ablation because of the characteristic rippling of silicon when subjected to pulsed laser irradiation [29]. This rippling suggests a mechanism whereby heat is transferred by thermal conduction to the graphene layer, causing its damage and/or ablation. This effect is evidenced by the appearance of a strip of different morphology in the area of laser incidence. It is not only observed in samples in which the substrate has been eliminated or damaged (figure 2, d-i) but also in the sample irradiated at ≈ 356 mJ/cm² (figure 2, c), the threshold energy density calculated for this graphene.

Figure 2. Optical images of graphene/Si/SiO₂ samples irradiated with nanosecond laser operating at different fluences. The images are ordered by increase fluence conditions (a) 31 mJ/cm², (b) 126 mJ/cm², (c) 356 mJ/cm², (d) 1030 mJ/cm², (e) 1450 mJ/cm², (f) 2180 mJ/cm², (g) 2818 mJ/cm², (h) 3477 mJ/cm², (i) 4240 mJ/cm².

In order to evaluate the extent of graphene damage, micro Raman mapping was applied to the samples. Figure 3 depicts the representative Raman spectra of the different regions. In general terms, three different regions can be observed (see S.D. for details). The first region corresponds to the ablation of the substrate (at fluences above ≈ 2180 mJ/cm²) and also to elimination of graphene at a fluence of ≈ 356 mJ/cm². The Raman spectrum is flat due to the absence of any carbon signal (figure 3: spectrum labelled ablated graphene). The second region is contiguous to the laser scribing path and its Raman spectrum corresponds to damaged graphene. This spectrum shows an increase in the intensity of the D band and a broadening of the 2D band similar to that of graphene oxide or oxygen-plasma treated graphene (figure 3: spectrum labelled damaged graphene). The third region corresponds to unaltered graphene that has not been affected by laser irradiation. In this case, the Raman spectrum is the same as that of raw graphene (figure 3: spectrum labelled perfect graphene).

Figure 3. Raman spectra (left) corresponding to three regions of the optical image (right) of the graphene/Si/SiO₂ sample irradiated by a nanosecond laser operating at a fluence of ≈ 2818 mJ/cm².

In order to study the evolution of defects on the sample, an analysis of the ratios of the D and G intensities ($I(D)/I(G)$) as a function of the distance (d) from the center of the laser spot was carried out. To obtain the maximum amount of information from these data, they were fitted to a stretched exponential, a function that is frequently applied for modeling of experimental relaxation data [30]. In this case, a strictly empirical expression (1) is proposed based on the stretched exponential function, given that it is well-known for being a simple analytical expression which allows an easy fit of the data gathered in this work.

Figure 4 shows the fit corresponding to a fluence of ≈ 1030 mJ/cm², which is representative of this type of laser patterning (see S.D. for details). The values were adjusted to the following expression:

$$\frac{I(D)}{I(G)} = A \cdot \exp\left(-\left(\frac{d}{D_0}\right)^\beta + B\right) \quad (1)$$

Accordingly, the curves $I(D)/I(G)$ vs. d were fitted to this function by using A , B , β y D_0 as free parameters for the adjustment.

Figure 4. Adjustment of a stretched exponential function of $I(D)/I(G)$ data vs. distance to the center of the scribe at a fluence of 2818 mJ/cm^2 .

It can be observed from the figure that $A+B$ is related to the maximum value of the $I(D)/I(G)$ (maximum density of defects) which is reached in the proximity of the scribe, while B corresponds to the minimum value to which this ratio tends over a certain distance, from which the effect of the laser is negligible. D_0 can be interpreted as the distance from the scribe edge to which this value (and therefore the number of defects in graphene) falls, and so it can be used to compare the effects of the laser in different conditions.

The parameters obtained for the rest of the laser conditions employed to scribe graphene are listed in Table 1:

Table 1. Parameters of the graphene patterning obtained from equation 1.

Fluence (mJ/cm^2)	A	B	$D_0, \mu\text{m}$
1030	0.774 ± 0.054	0.120 ± 0.047	39.13 ± 1.41
1450	0.715 ± 0.037	0.127 ± 0.029	36.86 ± 0.66
2180	0.724 ± 0.012	0.144 ± 0.009	20.86 ± 0.41
2818	0.846 ± 0.113	0.132 ± 0.074	17.85 ± 1.89
3477	0.880 ± 0.065	0.128 ± 0.040	16.25 ± 2.93
4240	0.902 ± 0.055	0.143 ± 0.015	14.46 ± 0.33

These results show that A and B remain almost constant, while the different values of D_0 obtained for the fluences show the evolution of the width of the damaged region with these conditions. This evolution is shown in figure 5 (blue bars).

Figure 5. Damage/ablation of graphene and substrate as a function of the fluences used for the irradiation of graphene/Si/SiO₂ substrates.

The results in figure 5 indicate that irradiation of the sample under the lowest fluence conditions (31 and 126 mJ/cm²) does not produce any damage either to the graphene or to the substrate. At a fluence of ≈ 356 mJ/cm² only the graphene appears to have been eliminated. Although an evaluation of the graphene fluence threshold lies outside the scope of this paper, it can be reasonably assumed to be at around ≈ 356 mJ/cm² for the graphene studied. At fluences of ≈ 1030 and ≈ 1450 mJ/cm² further ablation of graphene is expected. However, the Raman spectra evidence the presence of damaged graphene all over the zone irradiated by the laser. This sample also evidences damage to the substrate in the form of ripples, formed as a joint consequence of its partial melting (energy transport inducing heat-affected zone) and laser interference. This fact seems to modify therefore the ablation mechanism of graphene which, considering that the laser irradiation was performed under air, leads to oxidized graphene (higher ID/IG ratio of the carbonaceous spectra) due to thermal effects. It is suggested that the scribing process generates heat and that this heat is transferred by thermal conduction to the graphene layer. The ablation of graphene undergoes modification with thermal conduction causing damage (oxidation) to the surface of the graphene. Moreover, above ≈ 2180 mJ/cm² the removal of graphene is evident in exactly the same area where the substrate has been ablated, suggesting that it is the ablation of the substrate that causes the the elimination of the graphenic material and not the direct ablation of the graphene. Although, it cannot be discarded that C-C bond breaking by phonon energy might occur at some stage, it seems clear that the strong interaction between the graphene and the substrate is the prime cause of the graphene ablation process. This is also supported by the presence of damaged graphene in the zone adjacent to the scribe.

To assess the nature of the damage caused to the graphene by laser irradiation, the samples were analyzed by means of XPS prior to, and after, laser irradiation at a fluence of ≈ 2180 mJ/cm². The results, depicted in figure 6, are representative of all the fluences studied in which oxidized graphene was observed. It should be mentioned at this point that XPS analysis was used as a qualitative tool for comparing the scribed substrate and the untreated substrate. An analysis of the XPS C1s curves obtained indicates an increase in the amount of oxygen containing functional groups after laser irradiation. Since the laser irradiation is performed under air, this is

consistent with oxidation processes taking place in the graphene layer and matches well with the Raman spectra of the damaged graphene observed, suggesting the formation of oxidized graphene.

Figure 6. XPS C1s curves of the (a) untreated and (b) laser irradiated graphene on Si/SiO₂ at a fluence of 2818 mJ/cm².

It can be said that these results can be in accordance with a two-temperature model (TTM) [31] that leads to the oxidation of graphene (as observed by XPS) and heat diffusion to layers underneath (SiO₂/Si). In the same way, this model also predicts higher ablation thresholds for long pulses what corresponds well with our results. In any case, the interpretation of these results under TTM would precise a deeper understanding, combining TTM, optical and thermal modelling of the graphene/SiO₂/Si complete system, what clearly is out of the scope of this paper.

4. Conclusions

We have demonstrated in this work that graphene samples supported on Si/SiO₂ substrates can be easily patterned by means of green nanosecond pulse laser irradiation (532 nm). Raman spectroscopy showed that the multiple pulse ablation threshold fluence for selectively patterning the graphene was around 356mJ/cm², a value within the range of those reported by others using similar laser conditions. However, at higher fluences, the ablation of the substrate is direct, unlike the ablation of the graphene which is due to thermal phenomena because of the contact between substrate and graphene.

At fluence values of 1030-1450 mJ/cm² damage to the substrate was observed. In these cases, ablation of the graphene did not occur. However, the graphenic structure was modified over an area larger than that of the damaged substrate. The increase in the number of oxygenated functional groups in the regions measured by XPS suggests that this extended damage was probably caused by thermal phenomena during the ablation of the substrate.

Only the fluences that led to the ablation of the substrate caused the elimination of graphene over an area similar to that of the ablated substrate. Additional damage to the edge of the graphene sheet was also observed. It can therefore be reasonably assumed that elimination of the graphene was caused by the removal of the substrate and not by the direct ablation of the graphene.

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