Interaction of CVD Graphene with Pulsed Laser Illumination

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Nowadays, there is a frantic activity worldwide to exploit the unique optical properties of graphene and other 2D crystal materials in photonic applications ranging from solar cells and light-emitting devices to touch screens, photodetectors and ultrafast lasers [1]. On the other hand, it has been recently shown experimentally that two-photon absorption in graphene is an extremely intense phenomenon [2]. Moreover, graphene is an ideal memory material because of its transparency, conduction properties and solution processability [3]. In this line, a novel technique for 3D optical data storage is proposed. The memory material will consist of a stacking sequence of a building block, a PMMA layer with thickness of ~1μm in which stacks of graphene are attached on opposite sides. Defects induced in graphene upon pulsed laser illumination will be used as the recording mechanism in the proposed 3D optical memory.

In a first step, we examine the generation of defects on CVD graphene deposited on the top of Si/SiO_2 substrate, at normal conditions. The graphene lattice is illuminated using 80 fs pulses centered at 820 nm and a repetition rate of 80 MHz (laser spot ~1 μm) with different experimental parameters such as laser power and exposure time in order to create defects having the appropriate size to provide clear detection and high storage density. The illuminated samples are characterized by SEM imaging as well as Raman spectroscopy using the laser excitation of 514 nm and a 100x objective yielding 1 μm laser spot size. The laser power is adjusted carefully to prevent any thermal effect on the graphene.

Detailed Raman mapping of graphene took place before and after the laser illumination. The Raman spectrum of pristine graphene consists of two distinctive features, known as G and 2D peaks which are located at around 1580 and 2680 cm^{-1}, respectively. The presence of defects gives rise to other two features at around 1350 cm^{-1} (D peak) and 1615 cm^{-1} (D` peak). The Raman spectra identify the different types of damage on graphene from femtosecond laser interaction. Two different types of damage can be found on graphene from femtosecond laser interaction: (a) material degradation involving oxidation and/or formation of disordered carbon or carbon species, and (b) complete or partial ablation [4,5]. The I(D)/I(G) ratio has been widely used to evaluate the amount of disorder (or inter-defect distance, L_D) in graphene samples. The defected areas exhibit much higher I(D)/I(G) ratio compared to the non-defected ones indicating successful generation of defects (Figure 1a). The ratio between the D and G intensities for a given density of defects depends on the laser excitation energy. For all excitations, the D to G intensity ratio reaches a maximum for an inter-defect distance of ~3 nm [6].

Electronic microscopy and spectroscopy give similar results concerning the size and shape of the defected areas. The defected regions can be easily identified by SEM images (Figure 1b). Focusing on the defected areas, three different regions can be observed through significant contrast differences, out of the illuminated area, at the periphery of damaged region and within the damaged region. Increased laser power (ranging from 1 to 12 mW) leads to simultaneously increased defect size for a given exposure time of 20 sec. Laser power is not the only parameter that affects the size of the defected areas; by varying the exposure time (from 1 up to 100 sec) at the relatively low laser power level of 2 mW defected regions of different size can also be obtained. The higher the exposure time the higher the characteristic length of the defected areas. In any case, the laser fingerprint on graphene is nearly elliptic.

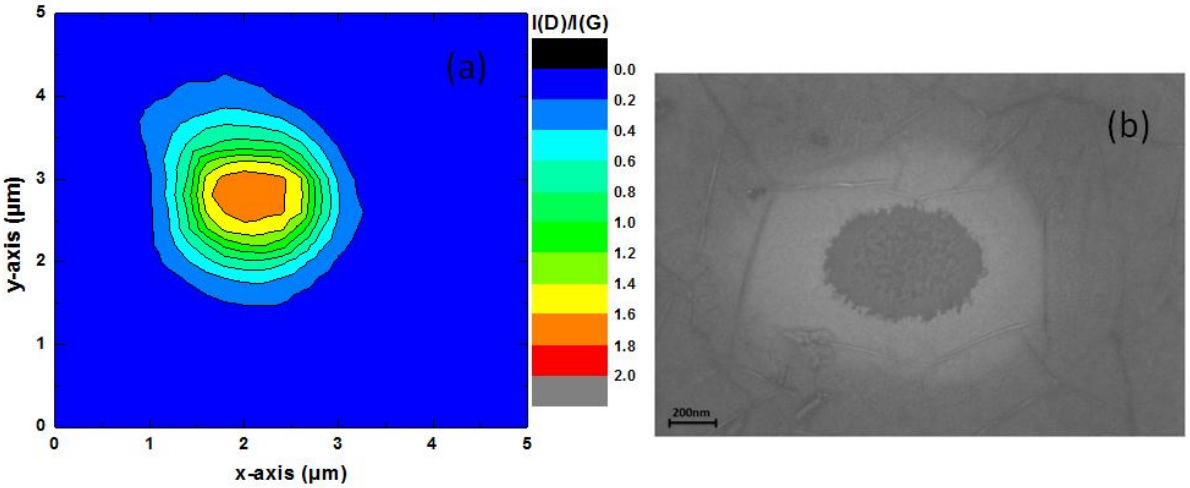

Figure 1. (a) Raman map of the D to G peak ratio measured with 0.2μm step of CVD graphene after illumination with 3mW laser power for 20sec and (b) SEM image of the same defected area.

Finally, we have measured by means of time-resolved pump-probe anti-Stokes Raman spectroscopy the relaxation rate of the G-mode of CVD graphene sample. The pump beam for excitation of the sample had an 816 nm central wavelength and it was supplied by an 85 MHz repetition rate with pulse duration of ~100 fs. The probe beam at 408 nm obtained by frequency doubling of the pump beam had almost the same pulse duration. A photomultiplier was used to detect the scattered light, which was first collected through a laser blocking bandpass filter and dispersed by a single-pass spectrometer equipped with a diffractive element of 1200 lines/mm. A G-mode lifetime of 1.2 ps at 300 K was measured. The results will be discussed in terms of possible decay channels of the G-band into phonons of other branches due to phonon-phonon interactions [7].

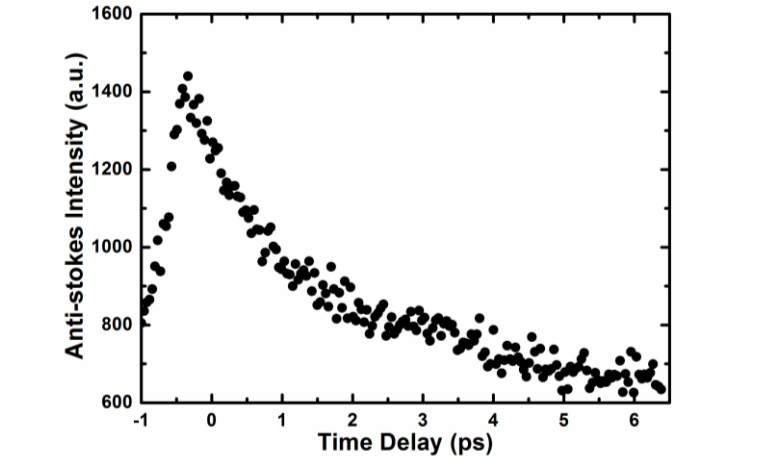

Figure 2. Anti-Stokes Raman signal for CVD monolayer graphene. The G-band signal is plotted as a function of the delay time Δt introduced between the pump (816 nm) and the probe (408 nm) beam.

References

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