Ultrafast Optical Kerr Effect method for the characterization of the third order optical nonlinearity of graphene

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Graphene, with its high and broadband optical nonlinearity, has attracted the interest of many researchers the last few years, as it appears to be a promising candidate for integrated photonics. In our work, we report the use of the ultrafast optical Kerr effect method with optical heterodyne detection (OHD-OKE) for the characterization of the third order optical nonlinearity of monolayer CVD graphene on quartz, at telecom wavelength. Our measurements show that the nonlinear refractive index of graphene is negative, in contrast to previously reported results. We also performed measurements of the nonlinear absorption of graphene and we studied the temperature dependence of the nonlinearity, as well as the relaxation time of the OHD-OKE signal.

Introduction

Since its theoretical prediction in 2008 [1], a lot of articles have been published about the large optical nonlinearity of graphene, focusing mainly on the saturable absorption, which is already used in mode-locked lasers. The nonlinear refraction of graphene has gained more interest in the last few years, namely because this 2D carbon sheet appears to be a promising material for integrated photonics. In 2012, the first Z-scan experiment on few-layer graphene [2] reported a positive nonlinear refractive index (n_2). Surprisingly, in our work published in [3] we found a negative n_2 for monolayer graphene from Z-scan traces. As both results were taken in the same lab, we checked our measurements with a robust experimental method based on the optical Kerr effect combined with optical heterodyne detection. In this way, we confirmed the negative nonlinearity of graphene [3] and discussed the possible reasons of the observed disagreement. Here, we extend our results and measure the imaginary part of graphene's nonlinearity, as well as its relaxation time.

Methodology

We used monolayer graphene grown by catalyzed chemical vapor deposition (CVD) on a Cu layer using CH_4 precursor. The graphene layer was transferred on a fused quartz plate and after that, Raman spectroscopy measurements demonstrated that the graphene is indeed a monolayer with high crystalline quality. Also, the sample was found to be slightly p-doped with a carrier concentration of a few $10^{12}\,\mathrm{cm}^{-2}$. These processes are described in [4]. We also used commercially available samples with the same characteristics.

The ultrafast OHD-OKE method [5, 6] is a pump-probe method mostly used in spectroscopy, in which the pump-induced birefringence or dichroism in a sample, is detected as a polarization change in the probe. The optical heterodyne detection not only improves the signal to noise ratio, but also enables the separate measurement of the real and the imaginary parts of the nonlinearity.

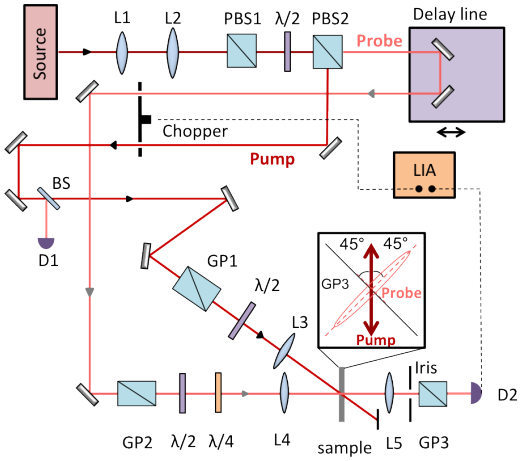

Figure 1: Experimental setup for the OHD-OKE method. The optical source is an OPO delivering 180-fs pulses at a 82 MHz repetition rate, at a wavelength of 1600 nm. The polarization of the pump and probe beams are tuned using the quarter- and half-wave plates (resp. $\lambda/4$ and $\lambda/2$) and the Glan polarizers (GP1 and GP2) in order to obtain the polarization states depicted in the inset. The ratio between the long and the short axis of the probe polarization state is $\tan\theta$. The chopper modulates the pump and the probe beams at different frequencies.

Our experimental setup is depicted in Fig. 1. The experimental procedure is described in detail in [3]. In a few words, in the simple OKE method, the polarization change due to the pump-induced nonlinear birefringence results in a non-zero field after the output Glan polarizer. In the optical heterodyne detection, for the measurement of the real part of the nonlinearity, we induce a small ellipticity in the probe by turning the half-wave plate a small angle θ, in order to get after the output Glan polarizer, a small field (local oscillator) with the same phase as the nonlinearly-induced field. The interference between the two fields results in the heterodyne term of the signal which is directly proportional to n_2. In order to measure the imaginary part of the nonlinearity, the output Glan polarizer is turned this time, to provide a local oscillator with the phase of the nonlinearly induced dichroism. In practice, we use a Lock-in amplifier to extract the OHD-OKE signal at the sum of the pump and probe chopping frequencies to avoid background signals and scattering. We measure the signal at different delays between the pump and the probe pulses for $\theta = \pm 4°$, and get the heterodyne part of the OHD-OKE signal by substracting the OHD-OKE signals obtained with opposite values of θ.

Results

We first tested our setup on a reference sample made of 1 mm thick pure silicon, with results being close to previously reported values [7]. The effective interaction length was $L \approx 100\,\mu$m, limited by the confocal length between the two beams. The OHD-OKE sig-

nals at $\theta = \pm 4°$ are shown in Fig. 2(a). Their FWHM corresponds to the autocorrelation of 180-fs laser pulses, indicating an ultrafast nonlinearity with electronic origin.

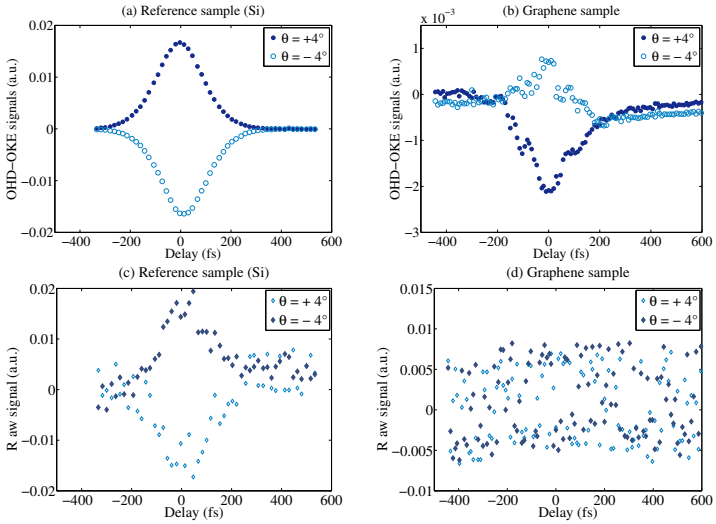

Figure 2: Experimental results from OHD-OKE: (a) OHD-OKE signal of reference sample (Si). (b) OHD-OKE signal of monolayer CVD graphene. We can see that the curves in (a) and (b) corresponding to angles θ present reversed signs. In (c) and (d) the same data but without Lock-in amplifier are illustrated for silicon and graphene respectively.

The OHD-OKE signals reported on Fig. 2(b) demonstrate clearly that the nonlinear refractive index of graphene is negative. The estimated value $n_2 \approx -1 \times 10^{-13}\,\mathrm{m}^2/\mathrm{W}$ has a magnitude compatible with [8]. Figs. 2(c) and (d) demonstrate the necessity of the Lock-in detection. We verified that the nonlinearity of the quartz substrate is not measured. In addition, we performed the same measurements at increased temperature until 375 K and we observed no sign change. We also annealed one of our samples and checked that the sign of the n_2 remained negative.

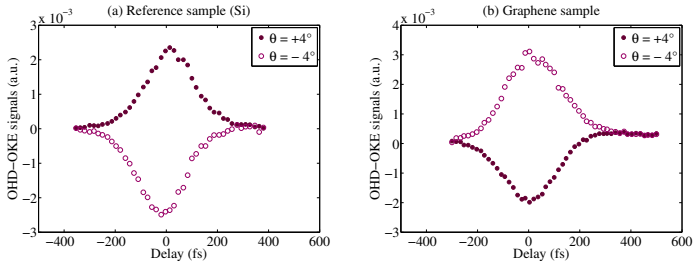

Figure 3: Experimental results from OHD-OKE imaginary part: (a) OHD-OKE signal of reference sample (Si). (b) OHD-OKE signal of monolayer CVD graphene. Again the curves in (a) and (b) present reversed signs.

Results for the the nonlinear absorption of Silicon are presented in Fig. 3(a). The nonlinear absorption coefficient corresponds to the imaginary part of the complex nonlinear refractive index $\kappa_2 = \mathrm{Im}\{\tilde{n}_2\} = \frac{\lambda}{4\pi}\beta$, where β is the two-photon absorption (TPA) coefficient. Again our values are in agreement with [7]. As for graphene, the signs are again reversed because in the range of pump intensities used, saturable absorption dominates in graphene. We get $\kappa_2^{eff} \approx -1.5 \times 10^{-13}$ m^2/W, where $\kappa_2^{eff} = \frac{\partial \kappa}{\partial I}|_{I_{pump}}$.

For both the nonlinear absorption and refraction, graphene presents a slower response than silicon. This is typical for graphene [9], however, its origin is not the induced birefringence (heterodyne part), but the nonlinear absorption of the local oscillator, which is consistent with [10, 11]. We measured relaxation times around 2 ps.

Conclusion

We experimentally demonstrated that the nonlinear refractive index of monolayer graphene is negative. We also measured a negative nonlinear absorption coefficient corresponding to saturable absorption and relaxation time around 2 ps.

Acknowledgements

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