Measurement of ultrafast carrier dynamics in multilayer MPCVD graphene

Tânia M. Ribeiro[1,*], *Tiago E. C.* Magalhães[1], *Bohdan* Kulyk[2], *Alexandre F.* Carvalho[2], *António J. S.* Fernandes[2], *Florinda M.* Costa[2], and *Helder* Crespo[1]

[1]Instituto de Física de Materiais Avançados, Nanotecnologia e Fotónica (IFIMUP), Departamento de Física e Astronomia, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[2]I3N, Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Abstract. Graphene presents unique opto-electronic properties which makes it useful for a wide range of applications and devices, such as high-speed photodetectors, that rely on the relaxation dynamics of photoexcited charge carriers. These demand reliable and reproducible methods for synthesis of high quality graphene. Here we present ultrafast degenerate pump-probe measurements of multilayer graphene coatings grown by microwave plasma chemical vapour deposition (MPCVD) and analyse the impact of the synthesis growth time on the material's nonequilibrium optical response.

1 Introduction

Ultrafast time-resolved spectroscopy techniques, such as pump-probe, can be used to study photoinduced dynamical processes in materials and in nanostructures [1, 2]. In pump-probe experiments, a first "strong" light pulse called pump promotes an electronically excited state. The temporal evolution of the photoexcited carriers can be observed by measuring the transmission of a second "weak" and delayed pulse called probe. The experiment holds information on the dynamic processes that occur in the system under study and has the advantage of probing the evolution of non-emissive or dark states. Understanding the carrier dynamics of graphene on a substrate is fundamental for the development of graphene-based optoelectronic devices [3]. The study of the dynamics can also reveal the quality of graphene, since, for example, the amount of defects in graphene affects its cooling properties [1]. In this work, we present preliminary ultrafast degenerate pump-probe measurements of graphene coatings synthesized by MPCVD. A range of graphene samples with an increased number of layers was studied. We will present the sample's characterization, the constructed pump-probe setup as well as the results for the relaxation dynamics of each sample.

2 Experimental Details

Graphene samples were grown by MPCVD on copper substrates using a procedure previously reported in [4]. Three samples, labelled as A, B and C, were submitted to different growth times: 0.5, 1 and 4 minutes, respectively. The laser used for time-resolved pump-probe spectroscopy is a commercial Ti:sapphire laser amplifier (Femtolasers Compact Pro CE-phase) with 1 kHz repetition rate, 800 nm center wavelength (~ 40 nm bandwidth), delivering sub-30 fs laser pulses with 1 mJ energy. Only a small percentage (~ 5%) of the laser power was fed to our home-built pump-probe system. Pump pulses, with an energy of 220 nJ were used to photoexcite carriers while probe pulses, with an energy of 7 nJ, were used to measure the differential transmission for different delays between the pump and probe pulses. Both beams were focused onto the samples with a spot diameter of ~ 80 μm. The polarization of the probe beam was rotated by 90 degrees with respect to the pump. An optical chopper was used to modulate the pump pulses at half the laser repetition rate. Besides blocking the pump beam, an additional spatial filter was used to block scattered pump light. The differential transmission in the

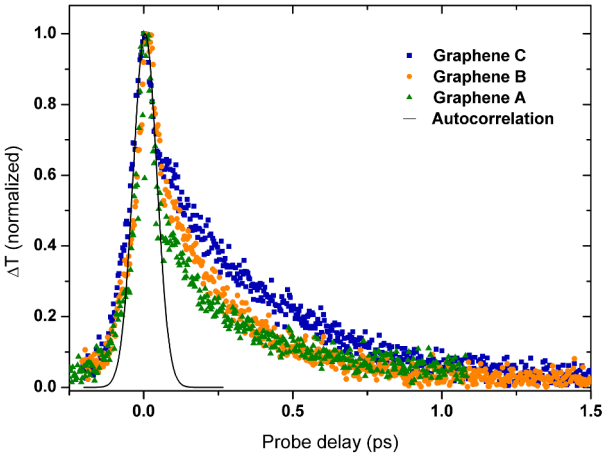

Figure 1. Measured differential transmission, ΔT, plotted as function of the probe delay for graphene samples A, B and C. ΔT is normalized at 1 for each graphene sample. The solid line represents the autocorrelation of the pump and probe pulses (full width at half maximum of ~ 90 fs).

*e-mail: tania.ribeiro@fc.up.pt

probe was measured with silicon photodiodes and a lock-in amplifier.

3 Results

Raman and UV-visible transmission spectra of the graphene samples indicated a variation in the number of layers proportional to the growth time. Therefore, the number of layers is proportional to the growth time and increases from A to C. Moreover, sample A presents an enhanced D peak in its Raman spectrum when compared to samples B and C, suggesting a larger degree of crystalline disorder [5]. The time-resolved response is shown in figure 1 for the three selected graphene samples (A-C). A bi-exponential decay model was used to fit the experimental data. The measured carrier relaxation time is on the order of 0.3 - 0.4 ps for the slower relaxation time (τ_2). The latter is attributed to interband scattering processes and was found to be proportional to the number of layers, i.e. decreasing from sample C to A. However, since defects can also accelerate the cooling process [1], a careful analysis with other complementary characterization techniques should also be performed.

References

[1] E. A. Pogna, A. Tomadin, O. Balci, G. Soavi, I. Paradisanos, M. Guizzardi, P. Pedrinazzi, S. Mignuzzi, K.-J. Tielrooij, M. Polini, A. C. Ferrari, G. Cerullo, ACS nano **16**, 3613–3624 (2022)

[2] R. Gatamov, A. Baydin, H. Krzyzanowska, N. Tolk, Materials Research Express **7**, 095601 (2020)

[3] M. Massicotte, G. Soavi, A. Principi, K.-J. Tielrooij, Nanoscale **13**, 8376–8411 (2021)

[4] A. F. Carvalho, T. Holz, N. F. Santos, M. C. Ferro, M. A. Martins, A. J. Fernandes, R. F. Silva, F. M. Costa, Carbon **98**, 99–105 (2016)

[5] J. M. Dawlaty, S. Shivaraman, M. Chandrashekhar, F. Rana, Michael G. Spencer, Appl. Phys. Lett. **92**, 042116 (2008).