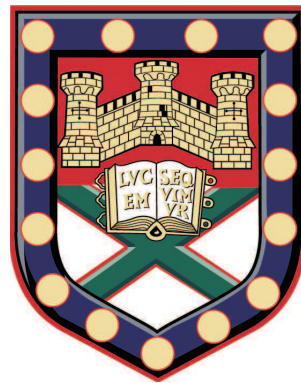


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Nonlinear and Nonequilibrium Optical Properties of Graphene



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A thesis submitted for the degree of
Doctor of Philosophy in Physics

2012

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Peter John Hale
2012

Abstract

In this thesis the nonlinear and nonequilibrium properties of graphene are experimentally investigated using degenerate four-wave mixing and time-resolved pump-probe spectroscopy. High quality exfoliated natural graphite and large area epitaxial graphene on silicon carbide are investigated with femtosecond and picosecond ultrafast pulses in the near-infrared. A bespoke technique for suspending exfoliated graphene is also presented.

In Chapter 3, the third-order nonlinear susceptibility of graphene is measured for the first time and shows a remarkably large response. Degenerate four-wave mixing at near-infrared wavelengths demonstrates an almost dispersionless emission over a broad spectral range. Quantum kinetic theory is employed to estimate the magnitude of the response and is in good agreement with the experimental data. The large susceptibility enables high contrast imaging, with a monolayer flake contrast of the order 10^7 times higher than for standard reflection imaging.

The degenerate four-wave mixing technique is utilised in Chapter 4 to measure the interface carbon signal of epitaxially grown graphene on silicon carbide. Comparable third-order signal from the silicon carbide bulk prevents true interface imaging. Excluding the third-order emission from detection by elongating the emission to outside a band-pass filter range allows for pure interfacial luminescence imaging. Features within the two growth faces are investigated with Raman spectroscopy.

Nonlinear measurements are an increasingly popular tool for investigating fundamental properties of graphene. Chapter 5 investigates the influence of ultrafast pulses on the nonlinear response of graphene. High instantaneous intensities at the sample are shown to reduce the nonlinear emission by a factor of two. Comparing the Raman peak positions, widths and intensities before and after irradiation points to a huge doping of the samples, of the order 500 meV.

In Chapter 6 the relaxation of photoexcited carriers is measured via time-resolved

pump–probe spectroscopy, where a layer dependence of hot phonon decay is observed. Single layer flakes are observed to relax faster than bilayers and trilayers, with an asymptote reached at approximately four layers. Removing the substrate and measuring fully suspended samples reveals the same trend, suggesting that substrate interactions are not the cause of the enhanced decay. The decay mechanism is therefore intrinsic to graphene, perhaps due to coupling to out-of-plane, flexural phonons. The thickness dependence of epitaxial graphene on silicon carbide is compared to that of exfoliated flakes where the layer dependence is not observed. Phonon relaxation times, however, are in good agreement.

Predictions for future investigations into this novel material based on the works here are suggested in Chapter 7. Preliminary pump–probe measurements at high carrier concentrations are an example of such progress, which will offer an insight into further decay mechanisms in graphene.

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