

# Directly Observing the Ultrafast Dynamics of Massive Dirac Fermions in Bilayer Graphene

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## Introduction

Graphene, the one-atom thick carbon wonder material that has sparked enormous interest in condensed matter physics and materials science research within the last 10 years, is considered a highly promising material in electronics and optics applications [1]. Unfortunately, it is not possible to switch off a current through monolayer graphene (MLG) due to the lack of a band gap, which is the essential ingredient in order to use the material in a logical device. This issue is elegantly solved if two layers of graphene are stacked on top of each other and if an electric field is imposed across such a bilayer [2]. However, previous transport measurements employing bilayer graphene (BLG) have shown that the resistance of the material is still too low, which is inconsistent with a small-gap semiconductor [3]. The underlying reason for this has been an ongoing mystery with studies pointing towards intrinsic structural defects in the material [4] or changes in the band structure induced by many-body effects [5]. Using the unique end-station for time- and angle-resolved photoemission spectroscopy (TR-ARPES) at the Artemis facility we have shed new light on this issue. With this method we have been able to directly track the movements of electrons within the bilayer graphene band structure with femtosecond time resolution when they are brought out of equilibrium with an infrared laser pulse. [6,7]

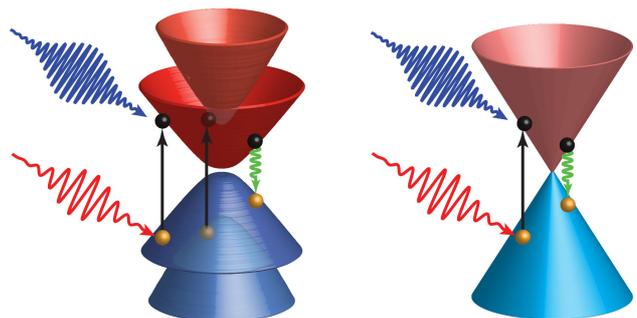
## Filming Dirac Particles with TR-ARPES

The hallmark of graphene is its electronic band structure, which consists of linearly dispersing bands that intersect at the charge neutrality point. Due to the analogy with the dispersion relation of photons the charge carriers in graphene are said to be massless Dirac Fermions, and the dispersion relation consists of a Dirac cone. Stacking two graphene layers leads to a very different situation - the dispersion relation then becomes characterized by two sets of paraboloids that are separated by a small gap. In the language of relativistic quantum mechanics this gap bestows the charge carriers with a mass, and they are therefore called massive Dirac Fermions. See Fig. 1 for a sketch of the BLG and MLG dispersion relations.

At Artemis we film these Dirac particles using a Ti:sapphire amplified laser system. Part of the laser beam is directed into a pulsed jet of argon gas atoms, which leads to high harmonic generation of XUV pulses. For this experiment we used the 13<sup>th</sup>

harmonic corresponding to 21 eV, enabling the photoemission of electrons from within the Dirac cone. The other part of the beam is used to excite the Dirac particles with an energy of 1.55 eV, bringing them from the valence to the conduction bands in mono or bilayer graphene. The relaxation of these excited charge carriers is then recorded using the XUV light with a time resolution of 40 fs, which makes it possible to directly observe carrier recombination involving e.g. lattice vibrations (phonons) or defects. The idea of the experiment is sketched in Fig. 1.

Our graphene samples have been grown on silicon carbide and decoupled from this substrate by intercalation of hydrogen. This ensures that the electronic structure closely mimics that of free-standing MLG or BLG. Furthermore, in the bilayer case the presence of the substrate yields a charge asymmetry between the two graphene layers leading to a small band gap [4].



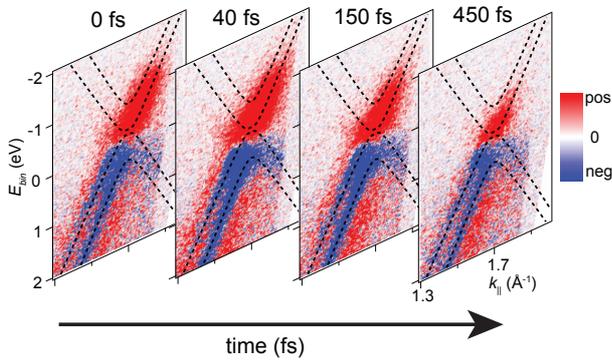
**Figure 1** Probing the dynamics of massive (left) and massless (right) Dirac Fermions in bilayer and monolayer graphene, respectively. An infrared pump pulse (red wiggled arrow) is used to move an electron (black sphere) from the valence bands (colored in blue) to the conduction bands (colored in red) thereby leaving behind a hole (yellow sphere) in the valence bands. Following this direct transition (shown by a black arrow) the relaxation of the electron is filmed using an XUV pulse (blue wiggled arrow) revealing electron-hole recombination processes (green wiggles).

## Ultrafast Thermalization and Interband Scattering

Snapshots of the measured ultrafast dynamics in BLG are presented in Fig. 2. These are difference spectra obtained by measuring the equilibrium ARPES signal before the pump reaches the sample and subtracting this signal from the spectrum obtained at a given time after the arrival of the pump.

The two parabolic valence bands of BLG are clearly resolved in the blue contrasts and provide an excellent match with a standard tight binding model. This shows that the out-of-equilibrium energy spectrum of BLG is correctly described within a single particle picture, and that the dispersion is not completely changed by many-body effects as suggested previously from transport measurements [5].

The distribution of excited electrons and holes is already smeared across the bilayer bands during the initial pumping stage i.e. around  $t = 0$  and  $t = 40$  fs. The charge carriers therefore thermalize via carrier-carrier scattering processes well within our time resolution, leaving behind a transient population of hot electrons. After 450 fs it can be observed that the inner conduction band has been depleted from these hot electrons as the intensity is now below the onset of this band. These cascade down to the outer conduction band efficiently via phonon-assisted interband scattering processes within the initial 200-300 fs.



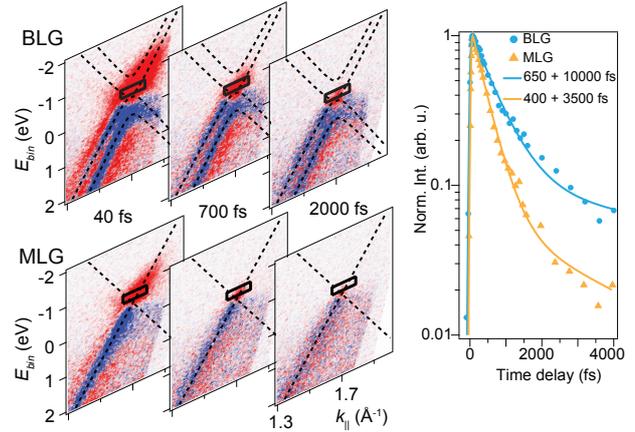
**Figure 2** TR-ARPES measurements of excited charge carriers in bilayer graphene. The spectra depict the difference between a spectrum taken before the pump beam arrives ( $t < 0$  fs) and the spectrum at the given time delay. Red therefore corresponds to electrons created via the pump, and blue corresponds to holes. The dashed lines are the single particle bands obtained from a tight binding calculation.

### Long-Lasting Hot Electrons in Bilayer Graphene

It is now an outstanding question what happens to the hot electrons once they accumulate at the bottom of the outer conduction band - does the band gap affect the carrier dynamics? Due to energy conservation electron-hole recombination across the gap becomes significantly hindered, because only the most energetic phonons can provide enough energy for such processes to occur. On the other hand, if midgap states due to structural defects [4] play a dominant role then such electron-hole recombination would occur efficiently via these defects, thereby short-circuiting the BLG band gap.

Here we approach this question by comparing TR-ARPES measurements of MLG and BLG, as shown in Fig. 3. We focus on the band structure region corresponding to the bottom of the conduction bands in the two systems i.e. the region marked by a black box in the spectra in Fig. 3. The intensity in this region is integrated and plotted as a function of time delay. A pronounced difference between MLG and BLG is clearly observed in the integrated intensity plot in Fig. 3, and by fitting the data by double exponential decays we find that the decay times in BLG are much longer than in MLG. Particularly, we find a slow decay with a time constant of 10000 fs, which merely sets a lower limit for the decay time because the decay is slower than the time window of the experiment. This dynamics is consistent with a gap in BLG that, compared to MLG, imposes a dramatic constriction on the hot electron relaxation near the conduction band bottom. This suggests that BLG could

be an ideal material for harvesting or storing energy in optoelectronic devices such as a solar cell, because the photoinduced charge carriers last for a long time in the excited state.



**Figure 3** Comparison of the dynamics in monolayer (MLG) and bilayer graphene (BLG). The dashed lines on top of the TR-ARPES difference spectra were obtained from tight binding models. The plot to the right shows the intensity integrated within the boxed region above the band gap (Dirac point) for BLG (MLG) throughout the considered time window. The data points correspond to measured data and the lines are fits to double exponential decays with the given time constants.

### Conclusions

Using the unique TR-ARPES method at the Artemis facility we have been able to directly observe the ultrafast dynamics of charge carriers in bilayer graphene. These so-called massive Dirac Fermions are well described by a single particle theory even in non-equilibrium conditions. The charge carriers cascade down to the bottom of the outermost conduction band within 200-300 fs, but here they get stuck due to a band gap. The relaxation across the gap is slower than the experimental time window, suggesting that BLG is a promising candidate for optoelectronic applications requiring excited charge carriers with a long lifetime. [7]

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