Journal of Electron Spectroscopy and Related Phenomena xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Ramifications of optical pumping on the interpretation of time-resolved photoemission experiments on graphene

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ARTICLE INFO

Article history:
Available online xxx

Keywords:
Graphene
Time- and angle-resolved photoemission
Space charge
Hot electrons

ABSTRACT

In pump–probe time and angle-resolved photoemission spectroscopy (TR-ARPES) experiments the presence of the pump pulse adds a new level of complexity to the photoemission process in comparison to conventional ARPES. This is evidenced by pump-induced vacuum space-charge effects and surface photovoltages, as well as multiple pump excitations due to internal reflections in the sample-substrate system. These processes can severely affect a correct interpretation of the data by masking the out-of-equilibrium electron dynamics intrinsic to the sample. In this study, we show that such effects indeed influence TR-ARPES data of graphene on a silicon carbide (SiC) substrate. In particular, we find a time- and laser fluence-dependent spectral shift and broadening of the acquired spectra, and unambiguously show the presence of a double pump excitation. The dynamics of these effects is slower than the electron dynamics in the graphene sample, thereby permitting us to deconvolve the signals in the time domain. Our results demonstrate that complex pump-related processes should always be considered in the experimental setup and data analysis.

1. Introduction

Angle-resolved photoemission spectroscopy (ARPES) offers a unique capability to investigate the electronic properties of quasiparticles in complex systems with energy and momentum resolution. Recent developments have seen significant advancements in adding femtosecond time resolution to ARPES in a pump–probe scheme [1–4]. New insights into the nature and origin of intriguing physical phenomena, such as collective excitations and phase transitions, can be gained by observing the time-dependent changes directly in the band structure. More specifically, time-resolved ARPES (TR-ARPES) gives access to the time-dependent changes of the spectral weight in selected states in the Brillouin zone. The different time scales observed connect to the different energy scales characteristic of the various kinds of interactions simultaneously present in the material [4]. Consequently, interactions felt by the quasiparticles in specific states can be disentangled by their characteristic time scales. This time, energy and momentum resolving capability is a virtue precluded to time resolved all-optical techniques. It has opened unprecedented possibilities to study the quasiparticle dynamics in a wide range of condensed matter systems, including the ultrafast amplitude oscillations in charge density wave materials [2–5], the quasiparticle recombination rate near the *d*-wave node in cuprate superconductors [1,6–8], the dynamics taking place on the Dirac cone

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http://dx.doi.org/10.1016/j.elspec.2015.04.010
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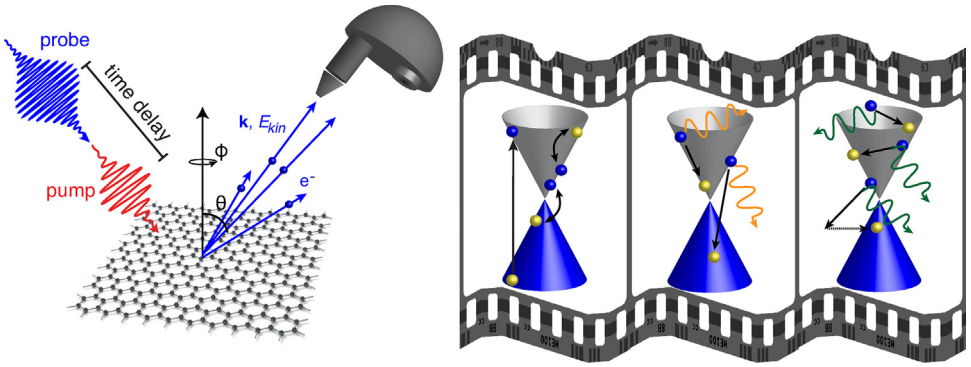

Fig. 1. Schematic of a TR-ARPES experiment on graphene. Electrons (blue spheres) excited by an infrared pump pulse are photoemitted by an ultraviolet probe on an ultrashort time scale and detected by an electron analyzer. This provides energy-, momentum- and time-resolved snapshots of the electron dynamics around the Dirac cone. Such measurements provide direct information about electron and hole (yellow spheres) recombination via electron–electron (curled arrows in left Dirac cone sketch) and electron–phonon (wiggled arrows) processes. Interactions between electrons and optical phonons (middle Dirac cone sketch), acoustic phonons and impurities (right Dirac cone sketch) can be disentangled by the time scales revealed in the non-equilibrium signal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in graphene [9–13] and on the surface of topological insulators [14–18].

In a TR-ARPES experiment the system in question is driven out of equilibrium via a femtosecond pump beam with an energy that is below the sample work function. After a variable time delay, the excited electron distribution is photoemitted using a second (probe) pulse with an energy above the work function threshold, as illustrated in Fig. 1 for the case of monolayer graphene. In a resonant pumping scheme, where the pump beam energy is resonant with the electron–hole transition energies in the materials band structure, the dynamics of the excited electron distribution and the accompanying spectral weight transfer is most often driven by electron–hole pair creation. Alternatively to this resonant pumping regime it is possible to couple the electromagnetic field of the pump beam directly to the electronic states of the sample and create special collective excitations. A prominent recent example of this is the observation of Floquet–Bloch states in a topological insulator driven out of equilibrium with a circularly polarized pump beam [19]. These dynamic states could be identified via the appearance of Dirac cone side-bands and a band gap opening at the Dirac point. Such states have also been predicted for graphene and TR-ARPES is the key experimental technique needed to find them [20].

The present work is centered around a study of photoexcited monolayer graphene using TR-ARPES. We focus on the resonant pumping scheme and monitor the relaxation of the excited electron–hole distribution in monolayer graphene back to the equilibrium state as the time delay is varied. This relaxation process involves a complex interplay of ultrafast electron–electron and electron–phonon scattering events. For monolayer graphene on SiC, several recent studies report that the initial thermalization of the excited carriers to a hot Fermi–Dirac (FD) distribution can be accompanied by a multiplication of the number of hot electrons with energies larger than the Fermi energy [12,21–26], and that the subsequent cooling of the hot electron distribution happens on different time scales determined by energy relaxation via optical phonons and acoustic phonons, primarily assisted by disorder-scattering (so-called super collision processes) [9,27–29]. These processes are sketched in Fig. 1 on the Dirac cones in movie snapshots.

To extract this intrinsic electron dynamics from the acquired TR-ARPES data, great care should be exercised as several experimental effects might influence the momentum and energy distributions of the photoelectrons before, during and after photoemission. In fact, in a low repetition rate laser source ($\leq$1 kHz) the intensity of both pump and probe pulses is necessarily high in order to detect a pump–probe signal out of the noise within a reasonable experimental time window. This implies a high electron density in the cloud of photoemitted electrons propagating toward the electron analyzer. The mutual Coulomb interactions between the photoelectrons create a vacuum space-charge effect that may lead to a shift of the electrons' kinetic energies and a severe broadening in energy that can easily exceed the resolution set by the light source and the analyzer [30–32]. Moreover, a very recent time-resolved X-ray photoelectron spectroscopy study by Oloff et al. [33] shows that photoelectrons emitted by the X-ray probe beam may also be influenced by the electric field originating from secondary electrons generated by the infrared pump. This may appear counterintuitive as the pump energy is typically lower than the sample work function (<4 eV). However, high-order nonlinear photoemission processes, where an electron simultaneously absorbs several photons, can provide sufficient energy for the electrons to escape into vacuum [33,34]. These processes can dominate in experiments with low repetition rate laser sources due to the requirement of high laser pump fluences on the order of 1 mJ/cm^2. For semiconductors, an additional effect, originating from a light-induced voltage difference in the surface region, can affect the propagating photoelectrons. Specifically, at the surface, the photoexcited electron–hole pairs can be spatially separated by the band bending. This separation generates a transient electric field that affects the photoelectron outside the sample. Despite having been known for several years, it was only very recently that the implications of this surface photovoltage (SPV) for TR-ARPES experiments were addressed theoretically by Tanaka [35] and experimentally by Yang et al. on semiconducting GaAs [36].

In this paper, we investigate the extent of these perturbing effects in the acquisition of TR-ARPES data from monolayer graphene on a semiconducting SiC substrate. We find strong indications of pump-induced electric fields and pump beam reflections at the backside of the SiC substrate that affect the measurement on picosecond time scales. A thorough understanding of these effects is important in order to suppress their impact on the experiment or deconvolve them from the intrinsic electron dynamics in the data analysis.

2. Experiment

The graphene sample investigated in this work was produced following a well-documented synthesis method that provides high-quality monolayer graphene on the Si-terminated face of SiC(0 0 0 1). The graphene layer was decoupled from the substrate by hydrogen intercalation [37,38] such that the structural and electronic properties probed by transport, Raman and ARPES

Please cite this article in press as: S. Ulstrup, et al., Ramifications of optical pumping on the interpretation of time-resolved photoemission experiments on graphene, J. Electron Spectrosc. Relat. Phenom. (2015), http://dx.doi.org/10.1016/j.elspec.2015.04.010