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Ultrafast electron dynamics in twisted graphene by femtosecond photoemission electron microscopy

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ABSTRACT

Twisted multilayer graphene (tMLG) present electronic properties that depend on the relative misalignment and interaction between layers. These interactions affect the band structures and the carrier dynamics upon photonic excitation. These structures are being under scrutiny and recent work high-lighted the strong potential they offer for optoelectronic devices. However, the ultrafast carrier dynamics is still at an early stage, often due to the instrumental limitations. Here, we investigated the carrier dynamics by femtosecond photoemission electron microscopy of chemical vapor deposited (CVD) twisted graphene super lattices presenting different interlayer rotation angles. The photo-generated carrier lifetimes in these selected regions show a longer lifetime compared to monolayer graphene (1 ML). This observation is assigned to the presence of band gap and sub bands in the trilayer graphene and has been supported by DFT calculations.

1. Introduction

Twisted multilayer graphene (tMLG) has attracted increasing attention owing their peculiar band structures. These stackings offer optical and electronic properties that could substantially improve the performance of optoelectronic devices [1–5]. A recent work by Tan et al. [6] proposed a way to fabricate large patches of twisted bilayer graphene (tBLG) with controlled rotation angle whereas Yin et al. [7] demonstrated using micro angle photoemission microscopy (ARPES) [8], the importance of the Van Hove singularities in twisted bilayer graphene to enhance the photocurrent generation in high sensitivity photodetectors [9,10]. Indeed, the recombination mechanisms are among the limiting factors for the performance of high-speed photo detectors and optoelectronic devices integrating nanoscale structures [11–13]. The recombination rate can be influenced by the intrinsic band structures of the graphene itself [14], but also by extrinsic factors such as structural defects. In particular, it has been reported that recombination rate increased from sub-picoseconds up to nanoseconds by introducing defect states from PMMA residues that typically occur during the transfer process [15]. The relaxation mechanisms have been extensively studied in various graphene types using optical pump probe techniques [15–20]. These techniques coupled with a femtosecond time resolution can capture the relaxation mechanisms in real time but do not offer sufficient spatial resolution to probe nanoscale regions. Ulstrup et al. [21,22] utilized time resolved ARPES (TR-ARPES) to probe the carrier dynamics in bilayer graphene [23]. The longer lifetime observed for the bilayer graphene compared to the monolayer is assigned to the band gap opening in AB stacked graphene layers. To date, the ultrafast kinetics of tMLGs have not been investigated and is therefore of particular interest. Here we couple an optical pump-probe technique using femtosecond (fs) laser pulses and a photoemission electron micros-copy system with the spatial resolution of 100 nm (time-resolved photoemission electron microscopy: TR-PEEM) [24,25]. We have already demonstrated the method for the study

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the photo excited carrier dynamics in a semiconducting GaAs substrate [26]. The space and time resolutions allow to monitor the relaxation mechanisms while focusing the analysis on a tMLG that exhibits a given rotation angle within a larger sample. This technique is a major asset for the study of the electron dynamics on real device heterojunctions. Man et al. [27] have recently employed TR-PEEM to measure the recombination lifetime of exfoliated InSe on GaAs substrate. Their results demonstrate the benefit of the technique for probing the electronic properties of semiconductors heterostructures [28–30].

In this work, we present the ultrafast dynamics in 1 ML and tMLGs CVD graphene super lattices. Our test structures are growth defects composed of twisted bilayer - trilayer graphene structures that appear in large-scale graphene grown by chemical vapor deposition (CVD) on copper (Cu). These structures present random twist angles that we have identified using Raman spectroscopy. Using TR-PEEM we observed the carrier dynamics, our spatial resolution allows to precisely locating the region of interest and therefore determined the recombination lifetime for different tMLGs. The tMLGs are particularly interesting for the measurement of the carrier lifetime as each of the regions identified presents different 2 ML and 3 ML interactions since they have different rotation angles. The question that arises is whether the carrier dynamics are twist angle dependent?

2. Experimental

The CVD graphene was grown on copper foil via chemical vapor deposition (CVD) method [31]. The copper foil was subsequently etched in $FeCl_3$ etchant and the graphene was transferred onto using PMMA resist. In order to ensure a clean surface on the superstructures and reduce the detrimental effect of residues on the data analysis, we have a carried out a thorough trichloroethylene vapor cleaning of the samples followed by DI water rinsing. The samples are subsequently annealed to evaporate the water. Subsequent Raman spectra (not shown) indicated a very low intensity D peak demonstrating the low defect density. We studied peculiar flower shaped structures present across the sample. These islands are mainly composed mono, bi and tri graphene layers and they were reported to occur when defects in the copper substrate trap the carbon atoms that are backscattered to the surface yielding to the formation of super lattices [32], Fig. 1(a). We have carried out AFM and HRTEM characterization on such structures, Fig. 1(b) shows the optical micrograph of a flower shape structure transferred onto 90 nm silicon oxide (SiO_2) where no residues can be detected on the superstructure. The diameter is about 14 μm and the central 3 ML region about 2 μm. The AFM profile superimposed on the image confirms the presence of mono (outskirt), bi (inner skirt) and trilayer (center) islands with 0.35 nm layer thickness. These structures are randomly distributed across the sample and each bi or trilayer present a different twist angle. Note that the SiO_2/graphene interface is free from residues as the PMMA is on the top layer constituted of graphene. We therefore expect a clean interface where only phonons from the SiO_2 could interfere with the bottom graphene layer during the recombination process.

Fig. 1(c) presents a fast Fourier transform pattern realized on the center of the twisted graphene structure. Angles α and β indicate the rotation angle between successive layers. Various tMLGs have been identified across the sample, Fig. S1 (supplemental information). The 1 ML graphene is p-type doped with a carrier density of 2.6×10^{12} cm^{-2}. The Fermi level is estimated to be 0.2 eV below the Dirac point. The mobility measured by Hall effect reaches up to

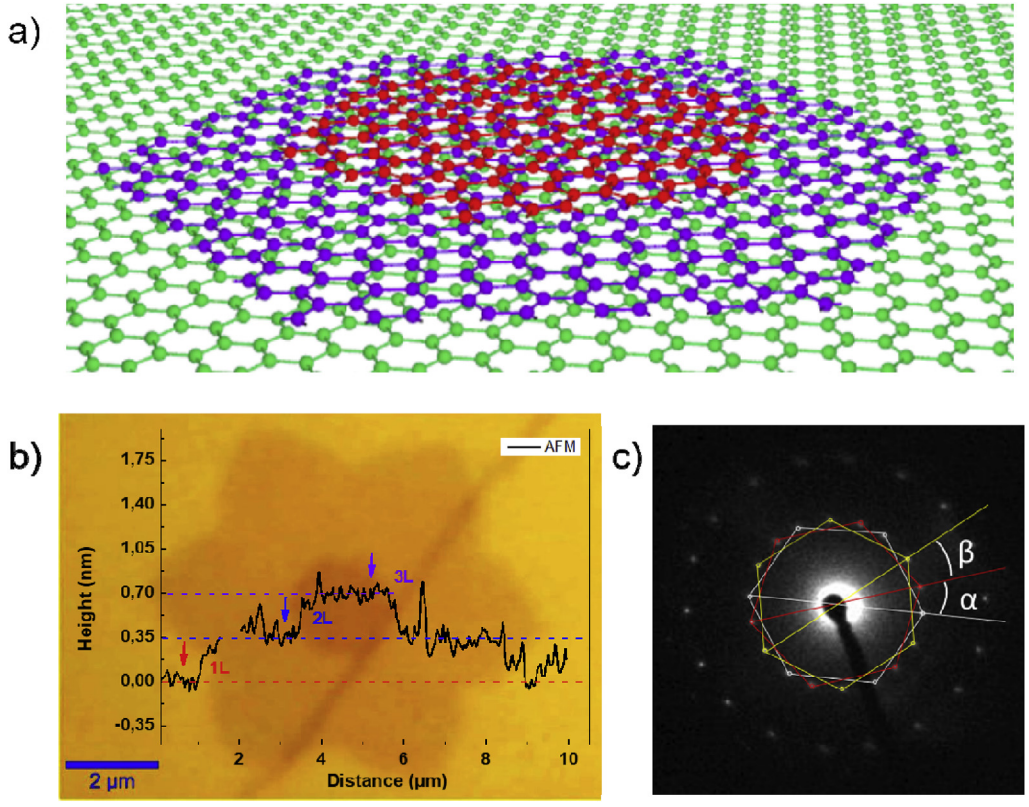

Fig. 1. (a) Conceptual drawing of the tMLG structure. (b) Optical image of a twisted graphene structure with the AFM trace superimposed indicating mono, bi and trilayer graphene. (c) Fast Fourier transform pattern of a typical twisted graphene structure Angles α and β are assigned to the rotation angle between successive layer. Note that the structures across the whole sample show a random distribution of angles. (A colour version of this figure can be viewed online.)