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High-Speed Spectroscopic Transient Absorption Imaging of Defects in Graphene

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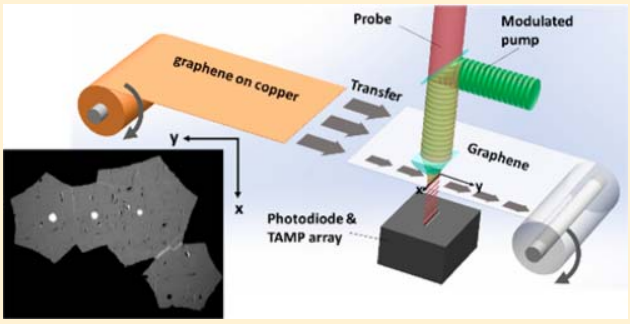
S *Supporting Information*

ABSTRACT: Graphene grain boundaries (GBs) and other nanodefects can deteriorate electronic properties. Here, using transient absorption (TA) microscopy we directly visualized GBs by TA intensity increase due to change in density of state. We also observed a faster decay due to defect-accelerated carrier relaxation in the GB area. By line-illumination and parallel detection, we increased the TA intensity imaging speed to 1000 frames per second, which is 6 orders of magnitude faster than Raman microscopy. Combined with a resonant optical delay tuner which scans a 5.3 ps temporal delay within 92 μs, our system enabled spectroscopic TA imaging, at a speed of 50 stacks per second, to probe and characterize graphene nanodefects based on the TA decay rate. Finally, we demonstrate real-time nondestructive characterization of graphene at a rolling speed of 0.3 m/min, which matches the fastest roll-to-roll manufacturing process reported.



KEYWORDS: *Graphene, grain boundary, ultrahigh-speed microscopy, transient absorption microscopy*

Graphene, a two-dimensional (2D) single atomic layer nanomaterial, is attractive for several applications, including future electronics, based on its outstanding electrical, mechanical, and chemical properties.[1] Large-area graphene films are achieved by chemical vapor deposition (CVD).[2,3] However, during CVD growth, nucleation of graphene occurs at multiple sites and each grows to island structures, consisting of one or more crystal orientations distinct from its neighbors. The islands intersect and form grain boundaries (GBs), which often present a unique change in the band structure and are viewed as inevitable defects.

Several methods have been developed for imaging GBs. Scanning tunneling microscopy (STM) has been reported as a reliable method for graphene GB analysis,[4] whereas the nanoscale resolution requires billions of pixels for micrometer-scale grain imaging. Dark-field TEM allows micrometer-scale grain imaging but with complicated sample preparation and requires specific substrates.[5] Raman microscopy can characterize graphene with both global properties (i.e., coverage, layer number) and local properties (i.e., GBs, nanodefects) based on the molecular vibrational spectrum,[6] but it necessitates an acquisition time of seconds per pixel. Thus, for in situ detection of nanoscale defects during the manufacturing process, a new modality that allows high-speed imaging of GBs and other defects in large-scale is needed.

When measuring graphene using transient absorption (TA) imaging, graphene electrons are excited by the pump from the valence band to the conduction band. The subsequent depletion of the valence band and pump-excited carriers inhibit the absorption of the sequential probe pulse due to ground state bleach and Pauli blocking, respectively, thus yielding a decreased absorption for the probe beam (Figure 1a). Experimentally, the pump laser is modulated in megahertz rate in order to reduce the $1/f$ laser noise. After interaction with the sample, the probe laser experiences intensity change at the same modulation frequency (Figure 1b). This small change of probe beam intensity, which can be extracted by a lock-in amplifier, enables visualization of the carrier density in the

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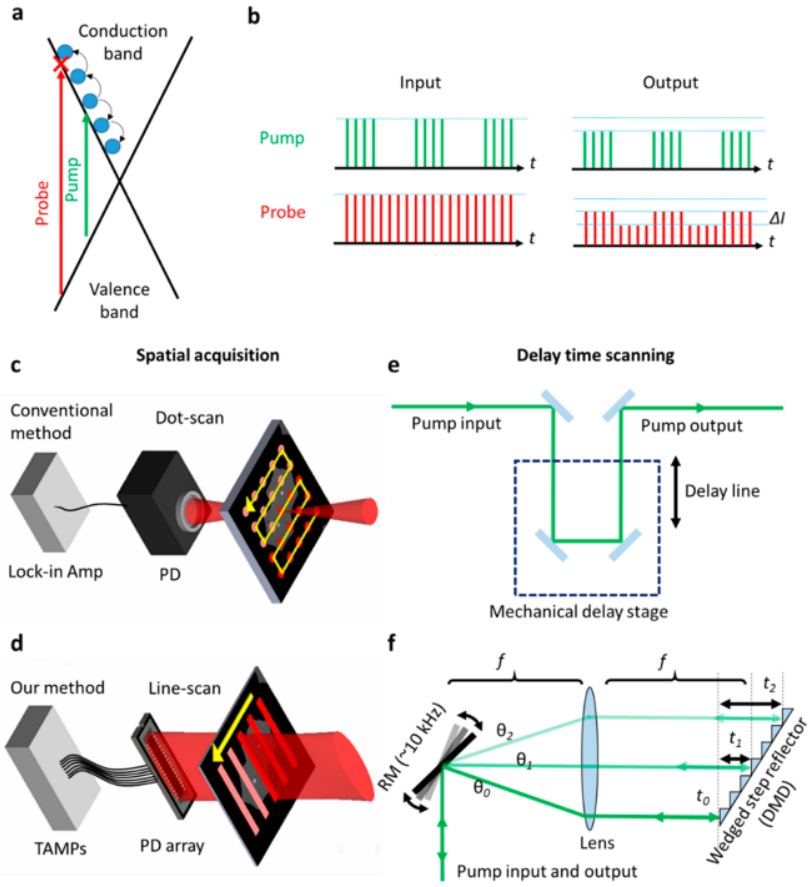

Figure 1. Principle and setup of ultrafast TA imaging of nanodefects in graphene. (a) Mechanism of TA process of graphene. (b) Modulation transfer from pump to probe beam due to TA process. (c) Conventional laser dot-scan in a raster pattern. PD: photodiode. (d) Line illumination and parallel detection by TAMPs improve acquisition time. PD array: photodiode array. (e) Conventional optical delay scan by a mechanical stage. (f) Resonant delay tuning improves the temporal resolution from several seconds to ~92 μs.

excited state. Time-resolved TA signal, obtained as a function of the optical delay of the pump and probe, provides insights on carrier relaxation dynamics in graphene.

Different time scale of the carrier dynamics in graphene has been studied by transient absorption measurement. First, the laser excites electrons from the valence band to conduction band as the "hot carriers". Within several tens of femtoseconds, electron−electron (carrier−carrier) scattering[7,8] leads the system to quasi-equilibrium. In hundreds of femtoseconds, the photoexcited carriers cool down by transferring energy to the lattice via intraband transitions by optical phonons, and interband transitions by radiative electron−hole (e−h).[9−11] In the following several picoseconds, the energy dissipates through acoustic phonon emission and the system arrives at thermal equilibrium.[12] However, the velocity of phonon is much slower than the velocity of electron. The momentum conservation constraint and velocity mismatch cause inefficient carrier relaxation through acoustic phonon emission.

Recently, Song et al. predicts another carrier relaxation pathway by the defect-assisted acoustic phonon scattering as the "supercollision" model. In this model, the collision between a carrier and both an acoustic phonon and a defect relaxes the momentum constraint and provides a faster energy dissipation process compared with acoustic phonon emission. Several experimental results of graphene are consistent with the SC model.[13,14] Therefore, TA decay curves is a hot-electron thermometer that records the cooling dynamics of hot electrons in graphene[15] and have been used to quantitatively characterize nanoscale defect density based on SC model.[16]

Here, we demonstrated that TA microscopy is able to visualize GBs, an important case of defects. We observed that in the TA intensity image at zero-time delay, TA signal increases at GB sites. We also provided insights on image mechanism. We show that TA intensity at GB sites increases because of changes in the density of states induced by disorientation of intergrains defects resulting in van Hove singularities. Thus, by matching the pump wavelength with resonances in the band structure, TA microscopy has the selectivity to image certain GB with different density of states. Meanwhile, in the TA decay mapping processed from time-resolved TA signal, the TA decay rate is faster at GB sites compared with single layer graphene area. The faster decay rate in GB area is consistent with the fact that defects in graphene accelerate the cooling of photoexcited carriers.

We further reported an unprecedented imaging speed for TA microscopy to enable real-time characterization of nanodefects in large-area CVD graphene. First, in order to improve the spatial acquisition speed by the conventional raster-scanning (Figure 1c), we deployed line-illuminated scanning scheme and parallel detection with a lab-designed tuned amplifier (TAMP) and photodiode array (Figure 1d). Our method allows TA imaging at 1000 frames per second at a specific temporal delay. At such speed, the surface coverage, degree of wrinkles, grain boundary, and layer numbers of graphene can be resolved with

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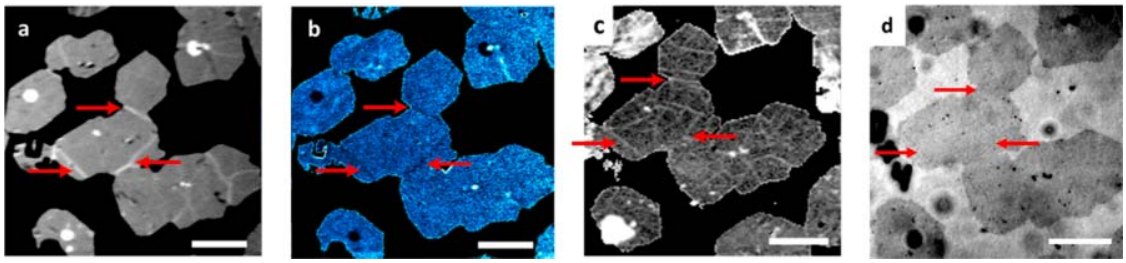

Figure 2. TA imaging of graphene grain boundary. (a) TA intensity image of grain boundary at zero-time delay. (b) TA decay mapping image of grain boundary from time-resolved TA signal. The darker area indicates faster decay rate. (c) Raman map of the ratio of the D peak (~1350 cm^{-1}) to the G peak (~1580 cm^{-1}). (d) The grain boundary is not visible in the conventional wide-field optical image. Scale bars: 20 μm.

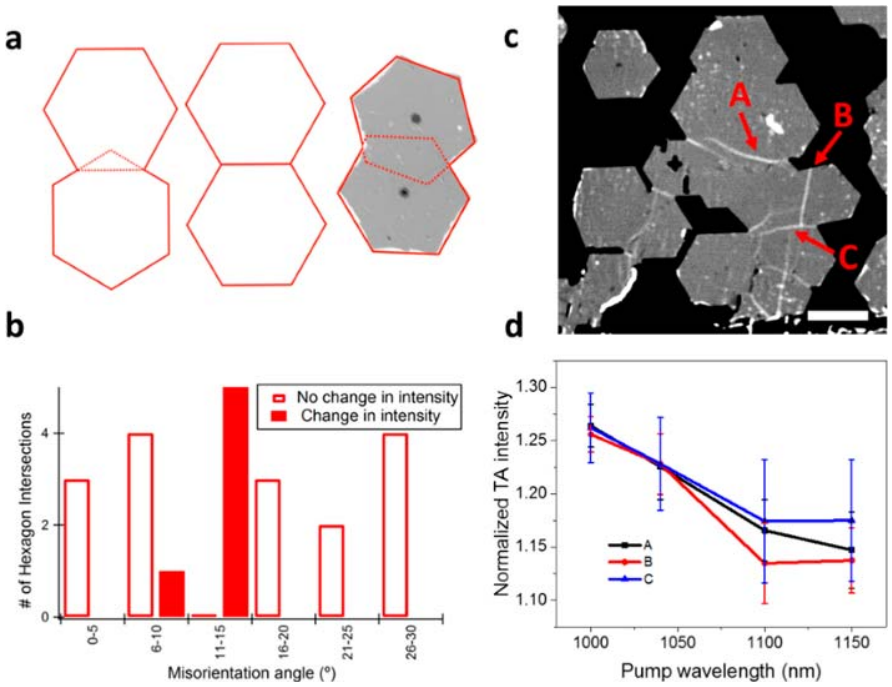

Figure 3. Angular dependence of graphene grain boundary. (a) Schematic of orientations of intersecting hexagons. (Left) Misorientation angle of 30°. (Middle) Misorientation angle of 0°. (Right) A representative fitting. (b) Histogram of intensity changes as a function of the misorientation angle. (c) Intensity map at zero-time delay (λ_{Pump} = 1040 nm). Scale bar is 20 μm. (d) Plot of intensities at noted features with varying pump wavelength. Probe wavelength is 810 nm for all data points.

35:1 contrast ratio of single layer graphene. Second, in order to improve the temporal delay tuning speed by conventional delay stage tuning method (Figure 1e), we integrated the resonant delay tuner with an angle-to-delay convertor (Figure 1f). We achieved acquisition of a time-resolved TA curve within 92 μs and decay mapping at the speed of 50 image stacks per second. Moreover, we are able to extract the density of nanodefects below the diffraction limit from the TA decay rate. Our technology enables high throughput characterization of graphene under the speed of 0.3m/min matching the state-of-art roll-to-roll manufacturing process.[31]

TA Imaging of Graphene Grain Boundary. Figure 2a demonstrates a TA intensity image where TA intensity signal at zero temporal delay between the pump and the probe is acquired at each pixel over a graphene sample synthesized by CVD method. Line features indicated by a higher TA intensity compared to that of single layer graphene areas are shown. Those intergrain structures suggest GBs. Figure 2b demonstrates TA decay mapping in the same area as in the Figure 2a. The slow decay time constant τ_2 in each pixel is extracted from a time-resolved TA signal and fitted with biexponential decay function. Because defects in graphene assist relaxation process of photoexcited carriers, the darker line features with faster decay rate can be assigned as GBs, as a structural disorder in graphene. We confirmed the assignment of GBs by Raman spectroscopic imaging of the same area (Figure 2c). We acquired Raman spectrum in each pixel and generated Raman image with the contrast of D peak to G peak intensity ratio. GBs were revealed with a higher D/G ratio, consistent with previous report.[6] The features highlighted by the red arrows in Figure 2a,b colocalized with higher D/G ratio in Figure 2c. Collectively, our results demonstrate that TA signal can be used for GB characterization with information comparable to Raman imaging. This GB site is not visible in a conventional wide-field optical image recorded from the same area of the same specimen (Figure 2d).

Via a detailed TA imaging study, we identified a few novel signatures of GBs. First, we noticed that GBs are distinct from other features which have similar dimensions, such as wrinkles. Specifically, Figure S1a shows the TA intensity of wrinkles and

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