

# Polymer Superstructure Dynamics on Free-Standing Graphene Resolved by Ultrafast Low-Energy Electron Diffraction

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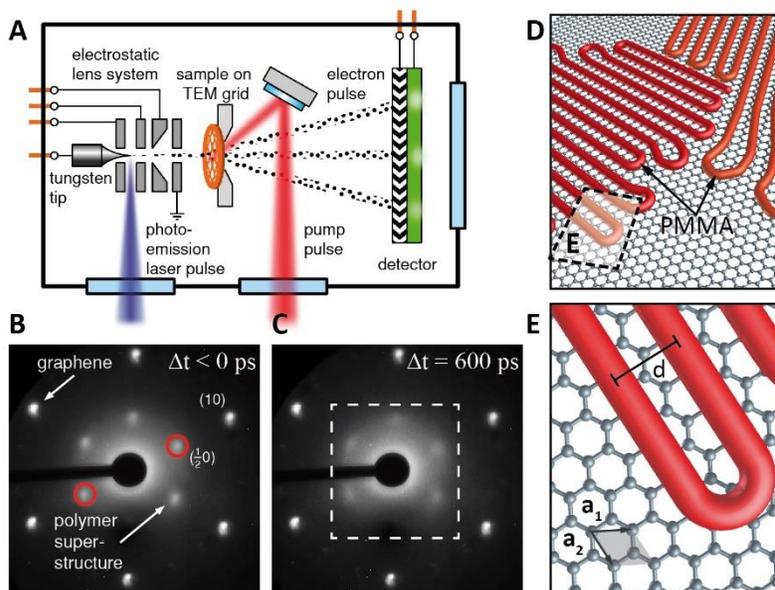
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**Abstract:** A newly developed technique for time-resolved surface science, ultrafast low-energy electron diffraction (ULEED), resolves the melting dynamics of a stripe-like polymer superstructure adsorbed on free-standing graphene.

**OCIS codes:** (240.6648) Surface dynamics; (320.7160) Ultrafast technology; (160.5470) Polymers

Ultrafast electron diffraction experiments have offered intriguing insights into atomic-scale dynamics on their fundamental time scales [1]. These techniques allow for the analysis of bulk systems and thin films with sub-picosecond temporal resolution. In contrast, comparable time-resolved studies at surfaces, interfaces and monolayer films remain largely elusive, despite recent accomplishments [2, 3]. However, such quasi two-dimensional systems are expected to show dramatically different behavior in comparison to bulk media, including unique phase transitions, surface reconstructions and adsorbate superstructures [4].

Here, we present a newly developed ultrafast low-energy electron diffraction (ULEED) setup [5]. In a first application, ULEED is employed to investigate the structural evolution in a freestanding polymer / graphene bilayer system. In particular, we resolve the interlayer heat transfer and superstructure melting dynamics in a laser-pump / electron-probe scheme (Fig. 1A). Due to the distinct mechanical, electronic and thermodynamic properties of the bilayer constituents, this system can serve as a model system in the study of structural relaxation in graphene-based heterostructures [6].

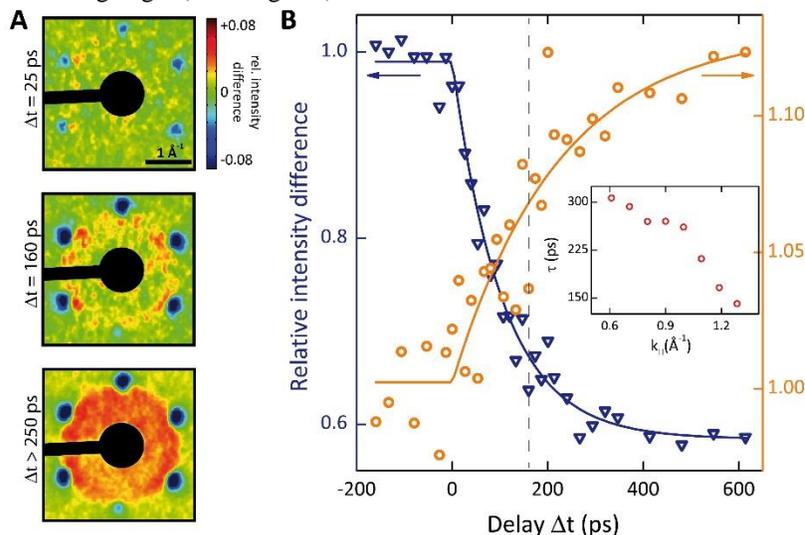


**Fig. 1:** ULEED setup and polymer/graphene bilayer system. Pump fluence 6 mJ/cm<sup>2</sup>, pump wavelength 800 nm, electron energy 450 eV.

**A:** Schematic of the laser-pump / electron-probe setup. **B, C:** Diffraction image of polymer / graphene bilayer system before and after excitation, respectively. Red circles indicate spots from single superstructure domain (cf. configuration in E). Dashed rectangle denotes region of difference images displayed in Fig. 2A. **D:** Illustration of the stripe-like polymer superstructure configuration, with two out of three orientations. **E:** Magnification of area marked in D. Superstructure chain-to-chain distance  $d = 4.26 \text{ \AA}$ . Graphene unit cell indicated.

Figure 1B shows the diffraction pattern of the six-fold symmetric single-crystalline graphene, with additional spots close to the central beam stop (red circles). These additional peaks stem from the adsorbed ultrathin polymer

layer of atactic poly(methyl methacrylate) (PMMA), which forms a superstructure consisting of folded-chain crystallites registered to the free-standing graphene substrate (Figs. 1D-E) [7]. We found that this superstructure can be reversibly melted upon laser excitation above a threshold fluence of about  $3 \text{ mJ/cm}^2$ , a fluence at which no significant change in the diffraction pattern of the graphene substrate is found (Figs. 1B and C). Specifically, two features can be observed, namely the reduction of the PMMA diffraction spot intensity, and an increased small angle diffraction (red disc). This is accompanied by an inward shift of the remaining spot intensity. Figure 2A displays difference images (dashed rectangle in Fig. 1C) for various points in time, indicating distinct timescales for the evolution of the diffraction spots and disc. These features are analyzed quantitatively as a function of delay time (Fig. 2B), fluence level and scattering angle (inset Fig. 2B).



**Fig. 2: Time-resolved structural dynamics.** Pump fluence  $6 \text{ mJ/cm}^2$ , electron energy  $450 \text{ eV}$ . All shown intensities normalized to negative delay  $\Delta t < 0$ . **A:** Difference images for central region at several time delays. **B:** Delay-dependent superstructure spot (blue triangles) and disc (red circles) diffraction intensities. Dashed line marks  $160 \text{ ps}$  delay time. Inset: Time constants for small-angle scattering increase as a function of scattering momentum.

We interpret the findings as follows: In the unexcited state, the PMMA chains are registered to the graphene substrate, forming three equivalent superstructure domains of folded-chain crystals rotated by  $60^\circ$  with respect to each other. Upon excitation, energy is mainly deposited in the graphene, followed by an energy transfer to the polymer with a transfer time of about  $40 \text{ ps}$ , which is still well above the temporal resolution of the ULEED setup (presently about  $2 \text{ ps}$ ). On a time scale of about  $100 \text{ ps}$ , the polymer-substrate registration and the crystalline order are lost (Fig. 2B, blue triangles). This is accompanied by an accelerated expansion of the remaining crystallites up to  $25 \%$  relative to the unexcited state and by the appearance of amorphous components (Fig. 2B, orange circles). The relaxation of non-crystalline structures proceed over durations of  $300 \text{ ps}$ , as observed by the scattering-angle-resolved timescales (inset of Fig. 2B). The different characteristic time constants can be understood as a direct result of the hierarchy of intra- and intermolecular coupling strengths between the bilayer constituents, and cannot be extracted from equilibrium properties alone.

The ULEED approach shown here provides a versatile access to ultrafast molecular surface science, ultimately allowing for a translation of the full analytical capabilities of LEED into the time-domain.

## References

- [1] B. J. Siwick et al., "An atomic-level view of melting using femtosecond electron diffraction," *Science* **302**, 1382-1385 (2003).
- [2] S. Schäfer, W. Liang, and A. H. Zewail, "Structural dynamics of surfaces by ultrafast electron crystallography: Experimental and multiple scattering theory," *J. Chem. Phys.* **135**, 214201 (2011).
- [3] A. Hanisch-Blicharski, A. Janzen, B. Krenzer, S. Wall, F. Klasing, A. Kalus, T. Frigge, M. Kammler, M. Horn-von Hoegen, "Ultrafast electron diffraction at surfaces: From nanoscale heat transport to driven phase transitions," *Ultramicroscopy* **127**, 2-8 (2013).
- [4] J. M. Kosterlitz and D. J. Thouless, "Ordering, metastability and phase transitions in two-dimensional systems," *J. Phys. Chem.* **6**, 1181-1203 (1973).
- [5] M. Gulde, S. Schweda, G. Storeck, M. Maiti, Y. K. Yu, A. M. Wodtke, S. Schäfer, and C. Ropers, "Ultrafast Low-Energy Electron Diffraction in Transmission Resolves Polymer/Graphene Superstructure Dynamics," *Science*, *in press* (2014).
- [6] A. K. Geim and I. V. Grigorieva, "Van der Waals heterostructures," *Nature* **499**, 419-25 (2013).
- [7] Y. Takanashi and J. Kumaki, "Significant melting point depression of two-dimensional folded-chain crystals of isotactic poly(methyl methacrylate)s observed by high-resolution in situ atomic force microscopy," *Phys. Chem. B* **117**, 5594-5605 (2013).