

Transient strain induced electronic structure modulation in a semiconducting polymer imaged by scanning ultrafast electron microscopy

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Abstract

Understanding the opto-electronic properties of semiconducting polymers under external strain is essential for their applications in flexible devices. While prior studies have highlighted the impact of static and macroscopic strains, assessing the effect of a local transient deformation before structural relaxation occurs remains challenging. Here, we employ scanning ultrafast electron microscopy (SUEM) to image the dynamics of a photo-induced transient strain in the semiconducting polymer poly(3-hexylthiophene) (P3HT). We observe that the photo-induced SUEM contrast, corresponding to the local change of secondary electron emission, exhibits an unusual ring-shaped profile. We attribute the observation to the electronic structure modulation of P3HT caused by a photo-induced strain field owing to its low modulus and strong electron-lattice coupling, supported by a finite-element analysis. Our work provides insights into tailoring opto-electronic properties using transient mechanical deformation in semiconducting polymers, and demonstrates the versatility of SUEM to study photo-physical processes in diverse materials.

Keywords: ultrafast electron microscopy, semiconducting polymer, strain effect, secondary electron emission, photoelastic effect

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I. INTRODUCTION

Semiconducting polymers are enabling materials for applications such as flexible optoelectronics [1, 2], solar cells [3], and bioelectronics [4]. The optical, electrical and mechanical properties of semiconducting polymers can be controlled by judicious design of their conjugated backbone and their sidechains [5]. Concurrently, the one-dimensional nature of the polymer chains is expected to give rise to strong coupling between the electronic states and the chain lattice, causing the formation of polaronic states upon the injection of charge carriers into a semiconducting polymer [6]. The strong electron-lattice coupling, in combination with the mechanical properties of polymers [7], signals the possibility of tuning the opto-electronic properties of semiconducting polymers via mechanical strain.

The effects of mechanical deformation on semiconducting polymers has been examined both by theory and experiment [8]. Computational studies show that structural disorder [9] and strain of polymer chains can modify their electronic structure [10]. The charge carrier mobility of semiconducting polymers has been experimentally shown to be modified by external tensile strain due to the change of interatomic distances, conformational changes, and chain alignment at large deformations [8, 11]. Compressive strain can have comparable effects with the optical gap of poly(3-hexylthiophene), P3HT [12], and other polymers [13] being strongly lowered by an external hydrostatic pressure. Thus, compared to their rigid inorganic counterparts, low-modulus semiconducting polymers provide an interesting platform to study the strain effect on the opto-electronic properties of materials.

One limitation of most existing strain studies of semiconducting polymers is that the applied strain is on a macroscopic length scale, usually using direct tensile testing, stretchable substrates, or mechanical indentation measurements [14–22]. In many experiments, a step of strain is applied to the sample for a relatively long time period [7]. While in the strained state, there can be structural relaxation in both ordered and amorphous domains of the polymer, which leads to changes in interchain distances and conformations before measurements of electronic properties. On the other hand, extensive time-resolved spectroscopic studies of semiconducting polymers have been performed, such as transient photomodulation [23], time-resolved photoluminescence [24], transient absorption [25], transient microwave conductivity [26], and transient grating [27] measurements. In these studies, however, the strain effect is typically a byproduct that is not systematically investigated. In this light,

to fully characterize the modulation of opto-electronic properties by strain directly applied to polymer chains, an ideal experimental technique would combine the following features: a high temporal resolution to probe the transient strain effect before significant structural relaxation occurs, a high spatial resolution to map local strain profiles, and a high sensitivity to detect the change of the local electronic structure.

Combining the time resolution of femtosecond lasers and the spatial resolution of electron microscopes, scanning ultrafast electron microscopy (SUEM) is a suitable technique [28–31] to image the spatial-temporal effect of photo-induced transient strain fields in semiconducting polymers. Besides the high spatial-temporal resolution, SUEM also provides extreme surface sensitivity [32], given the typical secondary electron escape length of a few nanometers. With these advantages, SUEM has been employed to visualize surface photocarrier transport across junctions [33, 34], hot photocarrier dynamics [35–38], and trap-mediated recombination [31], among other examples primarily in inorganic substances. Najafi et al. recently applied SUEM to image the photo-induced surface acoustic waves in P3HT on nanosecond and millimeter scales [39]. However, imaging the local impact of photo-induced transient strain on the electronic structure of semiconducting polymers on smaller time and length scales (picosecond and micrometer) has not been reported before.

Here, we demonstrate the space-time mapping of the dynamics of a photo-excited transient strain field in P3HT using SUEM. We measure the local change of the secondary electron emission as a result of photo-excitation, which gives rise to the SUEM image contrast. We observe a ring-shaped spatial profile with both bright and dark contrasts within the photo-illuminated area, indicating a nontrivial spatial distribution of the change in the secondary electron emission yield. The observed spatial profile develops with a rise time of ~ 300 ps, beyond which the profile persists up to the limit of the measurement time window (2.7 ns). We attribute the observed spatial profile to the local modulation of the electronic structure by a photo-induced radial strain that stretches or compresses the polymer chains aligned along the in-plane direction. This conclusion is supported by a finite element simulation of the dynamic elastic response of the polymer film to the photo-induced stress. We further discuss the origin of the stress and suggest it originates from photostriction, rather than thermal expansion. Our work demonstrates tailoring opto-electronic properties using transient mechanical strains in semiconducting polymers, and showcases the versatility of SUEM to study photo-physical processes in a broad variety of materials.

II. RESULTS AND DISCUSSION

A. SUEM Measurement

We employed SUEM to obtain time-resolved images of P3HT thin films deposited on thermal-oxide-covered doped silicon substrates. The procedure for sample preparation is identical to that in Ref. [40] and described in the Supporting Information Sec. II. A schematic of the SUEM setup is shown in Fig. 1(a) and the details of the setup are given in the Supporting Information Sec. III. Briefly, a fundamental infrared laser pulse train undergoes harmonic generations to create the visible pump beam (wavelength: 515 nm) and the ultraviolet (UV) photoelectron excitation beam (wavelength: 257 nm). The visible pump beam is focused onto the specimen to initiate a photo-physical process upon absorption. The UV beam is directed through the column of a scanning electron microscope (SEM) and onto the apex of a cooled Schottky field emission gun, generating electron pulses via the photoelectric effect [41], whose duration depends on the number of electrons packed within each pulse (see Supporting Information Sec. III for more discussion). The photo-generated electron pulses (the “primary” electrons) are accelerated inside the SEM column to 30 keV kinetic energy, and are finely focused to nanometer size through the electron optics in the SEM. Secondary electrons emitted locally from the sample surface upon the impact of the primary electron pulses are collected with a standard Everhart-Thornley detector (ETD).

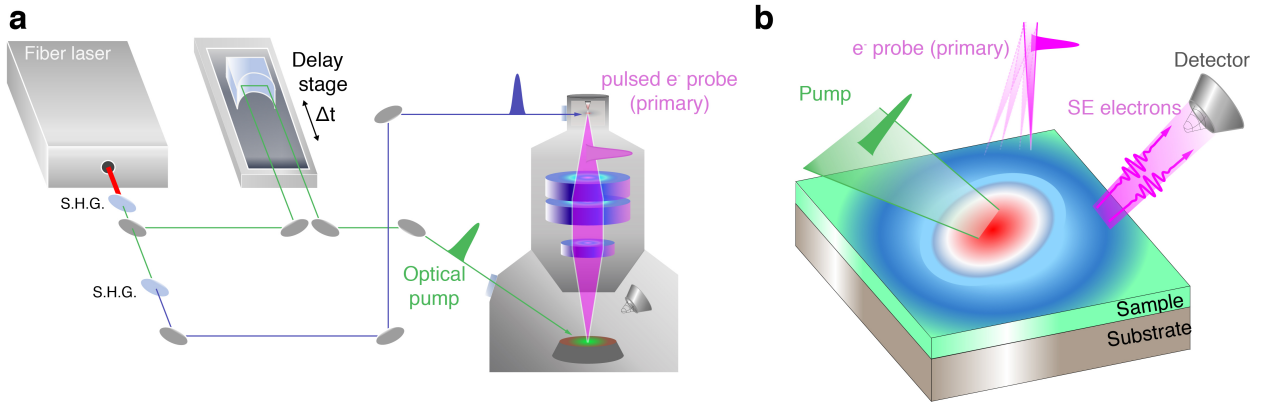


Figure 1. Schematic Illustration of the Experiment. (a) Schematic of the SUEM setup. (b) Schematic illustration of the SUEM image formation process.

Figure 1(b) further illustrates the optical excitation and the subsequent detection process.

The pump beam optically excites the sample, causing changes in the sample that can alter the secondary electron emission yield. The local change of the number of emitted secondary electrons is collected and used to form the SUEM contrast images. Time resolution is achieved by controlling the delay time between the optical pump pulses and the electron probe pulses using a mechanical delay stage. By monitoring the space-time evolution of the secondary electron contrast, the relevant photo-physical process on the sample surface can be directly visualized.

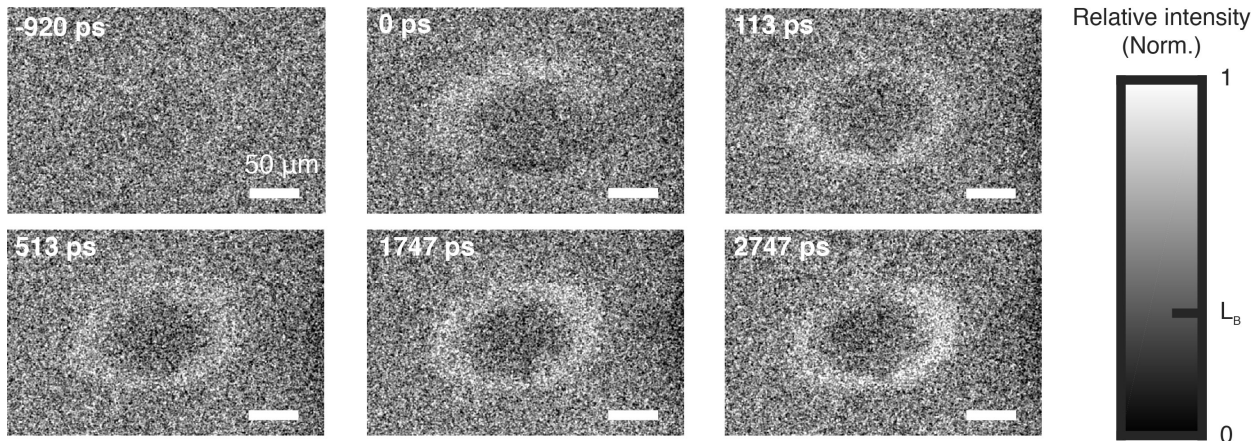


Figure 2. Representative Time-resolved SUEM Contrast Images of Neat P3HT Films at Several Delay Times. The optical pump fluence is $10 \mu\text{J cm}^{-2}$. A primary electron beam current of 80 pA was used for this dataset, corresponding to ~ 480 electrons per pulse given the repetition rate of 1 MHz. At each delay time, the measurements were conducted with the electron-beam dwell time of 100 ns and a few thousand scans were averaged to obtain each image. Subsequently, contrast images were formed by subtracting a reference image taken at -1.3 ns time delay. The measurements were conducted at multiple locations on the samples with various optical powers (see Supporting Information Sec. I for additional data). For visual clarity, a spatial Gaussian filter and a linear contrast stretching were used to process the raw images. The color bar indicates the normalized relative intensity distribution at each time delay, in which the L_B labels the average background intensity level.

B. Image Processing and Model Analysis

Figure 2 shows representative SUEM contrast images of a P3HT sample taken at different time delays. The dwell time of the electron beam at each pixel was 100 ns. The SUEM contrast images were obtained by subtracting a reference image taken at the pump-probe delay of ~ -1.3 ns when no photo-induced dynamics occur [33]. The laser repetition rate was set at 1 MHz to ensure the excited area returns to its initial state before the next pump pulse arrives. For visual clarity, the raw images were processed using a spatial low-pass Gaussian filter along with a contrast stretching with a linear intensity mapping. As shown in Fig. 2, we observe the generation of an initial spatial intensity contrast after the optical excitation. The horizontal diameter of the profile is ~ 100 μm , comparable to the incident laser spot diameter. A ring-shaped spatial profile with the bright contrast in the outer region and dark contrast in the center is clearly visible. The measured image contrast near the center of the ring is lower than the background level, indicating the photo-induced secondary electron emission yield near the center is lower than the surroundings without photoexcitation. While the intensity of the ring profile evolves with the delay time up to 2.7 ns, there is no obvious change of the shape of the spatial profile. We also conducted experiments with varying optical pump fluences and primary electron beam currents (see more data in Supporting Information Secs. I and III and movies). No qualitative difference was observed when the optical pump fluence was changed below ~ 12 $\mu\text{J cm}^{-2}$, while higher optical pump fluence led to photo-charging of the sample that would obscure the SUEM contrasts. We note here that the optical fluence used in our experiment is significantly lower than that used in previous SUEM experiments, which ranged from 20 $\mu\text{J cm}^{-2}$ [35] to 3000 $\mu\text{J cm}^{-2}$ [36].

We quantitatively analyzed the spatial-temporal evolution of the observed photo-induced contrast profile as follows. We first generated horizontal line-cut profiles from the contrast images as given in Figs. 3(a)-(d). We note the asymmetry in the background intensity at distances above ± 150 μm from the center, which arises from the fact that the distance from the ETD varies across the sample. This artifact was also observed in previous SUEM measurements [35] and needs to be considered when modeling the observed SUEM contrast. Next, we used a model to analyze the line-cut profiles in Figs. 3(a)-(d). Since the optical pump pulse has a Gaussian spatial intensity distribution, we heuristically considered an

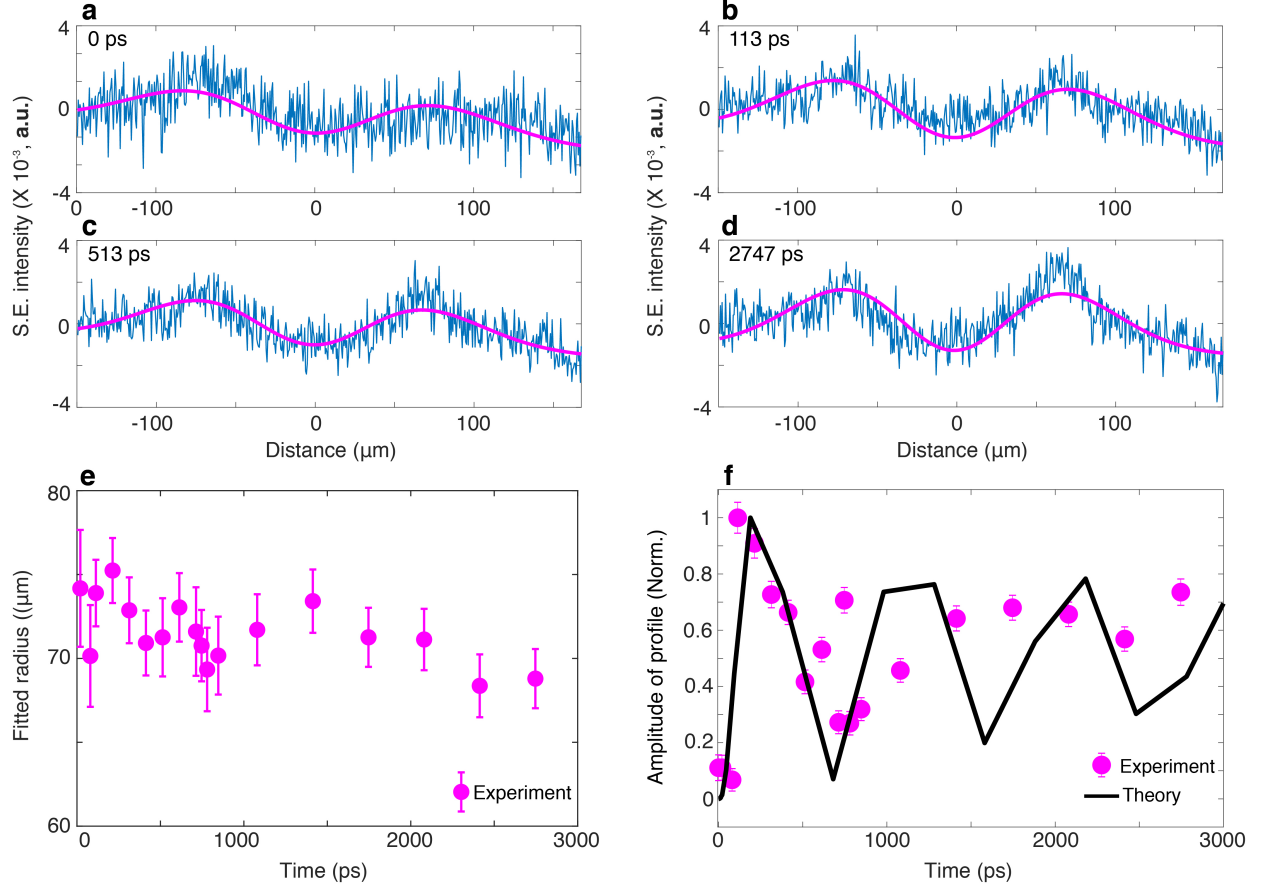


Figure 3. Quantitative Analysis of the SUEM Contrast Images of Neat P3HT.

(a-d) Measured horizontal intensity line-cut profiles at several delay times (blue lines), along with the best fits using the empirical model described in the text (magenta lines). The horizontal profiles are an average of the intensity along 40 pixel lines near the center of the photo-excited area. (e) Fitted radius of the spatial profiles versus the delay time. The radius corresponds to the parameter w in Eq. 1. The error bars were numerically determined with a 95% confidence interval. (f) Fitted amplitude of the spatial profiles versus the delay time. The error bars were numerically determined with a 95% confidence interval. Within the experimental uncertainty, the intensity rapidly increases below $\sim 200 - 300$ ps, above which the magnitude exhibits a periodic oscillation that is subsequently damped beyond 1 ns. The simulated amplitude of the radial strain versus time using a finite element method is given as the solid black line to compare to the experimental results.

empirical function that qualitatively captures the observed spatial profile with the following mathematical form:

$$f(r) = ar^2 \exp(-r^2/w^2) + mr + b, \quad (1)$$

where r is the radial coordinate, w is the radius of the spatial Gaussian distribution, m and b are parameters used to correct the asymmetric background due to the placement of the ETD, and a is the amplitude of the spatial profile. We used this model to fit the experimental line-cut profiles, shown as the solid lines in Figs. 3(a)-(d). The fitted parameter w , the effective radius of the photo-induced spatial profile, is shown in Fig. 3(e) as a function of the time delay. We observe that w remains relatively constant around the value of $\sim 70 \mu\text{m}$ after the spatial profile emerges upon photo-excitation within the time window considered in this work. In contrast to prior SUEM experiments [35–37], where the spatial diffusion of the photogenerated charge carriers was observed, the relative constant value of the radius w in our current work signals that the photocarrier diffusion was not captured within the measurement time window. This is consistent with the low diffusivity of photogenerated excitons and free charge carriers in conducting polymers including P3HT [26, 27, 42]. Despite the lack of a marked spatial diffusion, we observe nontrivial temporal evolution of the amplitude of the spatial profile, as shown in Fig. 3(f). We see an initial rise of the amplitude on the order of ~ 300 ps, followed by an oscillation of the amplitude with a period of ~ 1000 ps. More data on the amplitude evolution is provided in Supporting Information Sec. III, where these time scales are shown to be unchanged with different primary electron beam currents, signaling that the primary electron pulses are sufficiently short to resolve the dynamics. The amplitude oscillation implies that the observed spatial profile is related to the dynamic elastic response of the P3HT thin film initiated by a photo-induced stress. In fact, both the rise time and the oscillation time agree with a previous photoacoustic measurement of P3HT thin films [43].

C. Finite Element Simulation of Elastic Response

To verify this hypothesis, we simulated the dynamic evolution of an elastic strain field in a P3HT thin film after the photoexcitation using the finite element method (FEM) as implemented in COMSOL Multiphysics. We generated the initial stress profile assuming it originates from thermal expansion, although we later determined the amplitude of the thermal

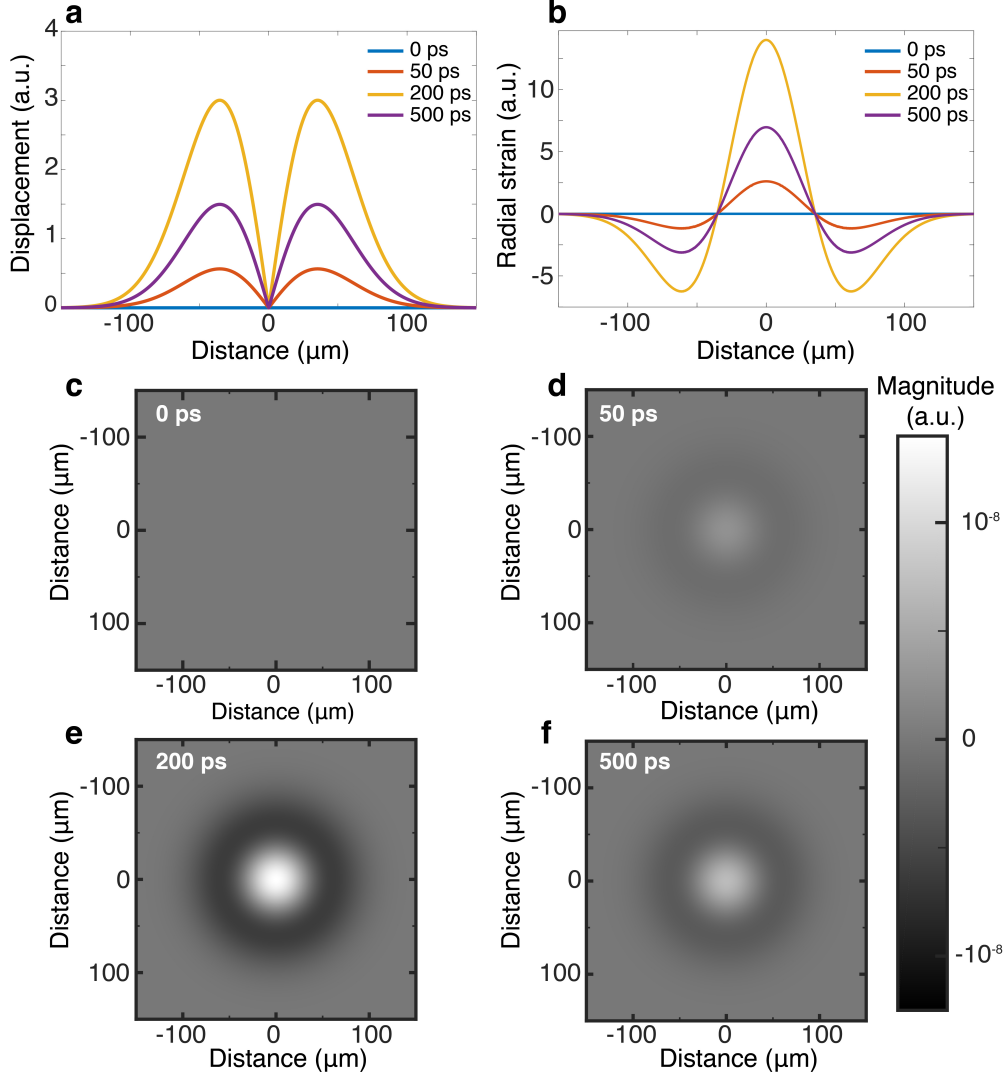


Figure 4. Calculated Transient Radial Strain after Photoexcitation using a Finite Element Analysis. (a) Calculated radial displacement versus the radial distance at several time delays. The origin indicates the center of the laser incidence spot (laser spot radius used: 50 μm). (b) The calculated amplitude of the radial strain versus the radial distance. The radial strain was obtained using the spatial derivative of the profiles in (a). (c-f) The simulated 2D radial strain distribution on the surface of a P3HT thin film at several delay times after photoexcitation. The experimentally observed ring-shaped profiles were reproduced in the simulation. The color bar indicates the amplitude of the strain.

stress was too small to explain the observed response (see Supporting Information Secs. IV and VI for details). However, since the subsequent linear elastic dynamics remain the same regardless of the origin of the initial stress, our simulation approach is justified. Given the

axial symmetry of the configuration, two displacement components were solved: the out-of-plane displacement u_z and the radial displacement u_r . Although u_z has a larger amplitude than u_r from the simulation, u_z follows a simple spatial Gaussian profile that cannot explain the experimental ring-shaped profile. The radial displacements u_r at different times are shown in Fig. 4(a). The characteristic spatial profile of the radial displacement is due to the zero-displacement boundary condition at the origin in an axial symmetric system. We further calculated the radial strain $\epsilon_r = \frac{du_r}{dr}$ that reflects the stretching or compression of the polymer chains along the in-plane direction. The resulting radial strain profile at the surface of the sample is shown in Fig. 4(b), in which the positive/negative strain corresponds to a tensile/compressive strain, respectively. We also plot the simulated two-dimensional profiles of the radial strain on the sample surface in Figs. 4(c)-(f). Physically, this radial strain profile reflects the tendency of the central region to expand after the photo-excitation while the radial displacement far away from the excited region remains zero, resulting in a compressively strained region near the edge of the photo-excited area. Furthermore, the simulated amplitude of the spatial profile as a function of time is compared to the experimental values in Fig. 4(f). The triangular waveform is characteristic of a thickness resonance excited in a thin film, as observed in prior photoacoustic measurements [44, 45]. However, a discrepancy between the experiment and the simulation can be seen, particularly beyond 1000 ps. A probable reason for the discrepancy is that the elastic damping and structural relaxation of the strained polymer film can occur at longer time scales, which were not included in the FEM simulation.

Several observations are worth a more detailed discussion. First, we note that the secondary electron yield is more sensitive to the radial strain than the out-of-plane strain. We attribute this observation to the anisotropic polymer chain alignment in a thin polymer film. It is well established that the chains in P3HT are dominantly aligned along the substrate in thin films [46]. Therefore, the in-plane strain should have a direct impact on the backbone while the out-of-plane strain mainly affects the interchain distance. Second, from our experiment, the observed bright contrast in the ring-shaped region under a compressive strain indicates that a compressive strain on the polymer chains enhances the secondary electron emission, while the dark contrast in the central region under tensile strain implies the opposite effect. This observation can be attributed to two factors. First, the band gap determines the minimum energy loss of a primary electron during the secondary electron emission pro-

cess [47]. Therefore, a smaller band gap indicates a wider range of possible energies for the generated secondary electrons and a higher secondary electron yield [47]. Optical measurements of P3HT under a hydrostatic pressure showed a reduced bandgap [12]. First-principles simulation of P3HT has also shown that a compressive/tensile strain reduces/increases the band gap [10], in agreement with our finding. Second, the ionization potential can also be changed by the strain: a quantum-mechanical simulation of a semiconducting polymer [48] has indicated that the ionization potential is lowered/raised by a compressive/tensile strain. Recently, the strong influence of both the electronic band gap and the ionization potential (and a related quantity - the electron affinity) on the secondary electron yield from P3HT has been demonstrated experimentally and via a Monte Carlo simulation [49, 50], showing qualitative agreement with our results. Third, we further investigated the origin of the photo-induced stress that initiated the dynamic elastic response. Due to the low excitation level, we estimated the temperature rise caused by the absorption of the pump pulse to be within 2 K and calculated the resulting thermal stress due to thermal expansion (see Supporting Information Secs. IV and VI for detailed discussion). We found the displacement induced by the thermal stress is exceedingly small and, thus, is unlikely to be responsible for the observed material response. Instead, we suspect the initial stress is directly induced by the generation of photocarriers and the strong coupling between the charge carriers and the polymer chains. This so-called “photostriction” effect has been reported in inorganic semiconductors [51], hybrid perovskites [52] and semiconducting polymers [53]. Our results suggest that, even at moderate photoexcitation levels ($\sim 10^{18} \text{ cm}^{-3}$ photocarrier concentration), the photostrictive stress along the polymer chains can be significantly higher than the thermal stress in P3HT. In comparison, conventional spectroscopic methods such as optical pump-probe techniques [43, 54] measure the average response of the material within the illuminated region and, thus, have not revealed the complex spatial strain profile. Furthermore, due to the relatively large optical absorption depth (tens to hundreds of nanometers), conventional optical spectroscopic methods are more sensitive to photo-induced changes in the bulk, e.g. the thickness change due to the out-of-plane displacement. In contrast, SUEM has superior surface sensitivity due to the small secondary electron escape length (typically few nanometers), and thus, is more sensitive to the surface radial strain.

III. SUMMARY

In summary, we report SUEM measurements of the space-time responses of the semiconducting polymer P3HT after photo-excitation. Combining an empirical model and an FEM simulation, we attribute the observed ring-shaped spatial profile to the local modulation of the polymer’s electronic structure by a photo-induced radial strain. The radial strain compresses or stretches the polymer chains along the in-plane direction, which changes the electronic structure of the polymer due to the electron-lattice coupling. We further suggest that the major contributor to the observed radial strain is the photostriction effect, rather than thermal stress. Our results provide new insight into the strain effect in semiconducting polymers, and demonstrate the versatility of the SUEM technique.

SUPPORTING INFORMATION

Additional SUEM data and analysis, sample preparation, characterization, instrumentation and modeling details. This material is available free of charge via the internet at <http://pubs.acs.org>.

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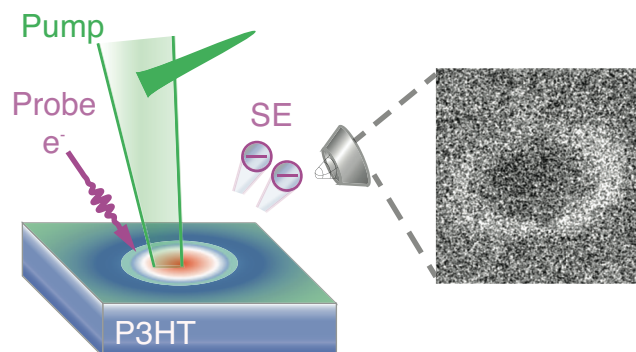


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