Defect-initiated formation mechanism of 3D carbon tracks on flexible transparent substrates by laser irradiation

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ABSTRACT

Laser direct writing of 3D carbon structures onto flexible polymer substrates offers potential of rapid roll-to-roll manufacturing for a variety of key applications, including large area sensors, flexible electronics, robotics, energy storage/conversion, and other consumer applications. The specific formation mechanism of the carbon structures has been an issue of debate for many years with the prevailing notion of a simple photothermal conversion reaction that mainly depends on the total energy input. However, this view has been shown to be inconsistent with experimental observations of nonlinear changes in the resulting structures when multiple processing parameters are simultaneously changed. In this study, we propose a formation mechanism based on the nucleation and growth of laser-induced defects, which is experimentally validated by irradiating a continuous wave laser beam onto polydimethylsiloxane. The model is further validated by intentionally introducing controlled defects by femtosecond laser irradiation, and indicate the implications of a two-laser laser direct writing technique to go beyond the current processing limits. These results clarify the previously ambiguous mechanisms by which carbon structures form under laser irradiation and provide a deeper understanding of how to control photothermal processes for advanced material processing.

1. Introduction

The development of processing techniques capable of the selective functionalization of polymer substrates enables the roll-to-roll manufacturing of a wide range of low cost, lightweight and flexible consumer products, from simple product labels to advanced wearable electronics [1–5]. Conventional processing techniques typically deposit prepared functional materials onto a target polymer substrate using, for example, a rigid stamp [6,7]. While these techniques are highly scalable, there has been a recent shift in demand from mass production to mass customization, in which on-demand processing capabilities are required to produce products tailored to individual needs [8]. Laser direct write (LDW) techniques are uniquely poised to answer these customized processing needs, since laser-based methods are highly controllable, fast, and straightforward to implement into mass production systems [9]. In the context of polymer modification, selective functionalization of polymer substrates can be achieved with high resolution and throughput [10]. Moreover, as the laser beam is digitally controlled, the beam path can be changed on the fly, offering high versatility, a benefit which is difficult to realize in conventional mechanical techniques.

The formation of spatially patterned 3D carbon structures on polymer substrates, or laser-induced graphitization, has applications ranging from unique identification tags [11,12], energy devices [13–15], and sensors [16–18]. In this technique, laser irradiation induces permanent photothermal changes to a polymer substrate, endowing it with attractive properties such as high optical absorption (>90 % for EUV to IR wavelengths), surface area (~340 m2/g), electrical conductivity (~5–25 S/cm), and thermal stability (>900 °C) [13,19,20]. Despite the versatility and scalability of this technique, a deeper understanding of the underlying photothermal mechanisms is required to exquisitely control the resulting morphology and properties. Recent attempts to understand the laser-material interactions involved individually changing the laser processing parameters, such as laser power, scanning speed, beam size, or scan number, to observe the structural evolution [12,13,20–23].
Based on this, the formation mechanism of carbon structures has been discussed to be a simple photothermal conversion reaction that is mainly dependent on the total energy input, or laser irradiance [24]. However, this simple mechanism is insufficient to explain the nonlinear changes in the resulting structures and properties when multiple laser processing parameters are simultaneously changed [25–28].

In this study, we reveal that structure formation is a highly complex, temporally- and spatially-dependent phenomena which cannot be explained solely by the laser irradiance, and elucidate the structural dependence of 3D carbon structures formed by the laser irradiation of polymers. Based on our findings, we propose and validate a mechanism based on the formation of laser-induced defects. We further present a two-laser LDW technique which significantly overcomes the processing limits for the patterning of 3D carbon structures. These results clarify the previously ambiguous mechanisms by which carbon structures form under laser irradiation and provide a deeper understanding of how to control photothermal processes for advanced material processing.

2. Experimental

2.1. Substrate preparation

Polydimethylsiloxane (PDMS) was chosen as the test substrate for this study as it is a well-known polymer with many attractive intrinsic properties, and also since it has been well-established to be a viable polymer precursor for laser-induced graphitization [29–31]. A 10:1 mixture of polymer to curing agent of PDMS (SYLGARD 184, Dow Corning, USA) was prepared. The mixture was drop casted onto a glass slab and degassed in vacuum to remove any air bubbles trapped during the mixing procedure. Furthermore, the mixture was cured in an oven at 80 °C for 60 min to prepare PDMS sheets. The PDMS sheets prepared in this study were approximately 1 mm in thickness. Before irradiation experiments, the surfaces of PDMS were washed with ethanol to remove any debris.

2.2. Laser irradiation

Continuous wave (CW) laser irradiation experiments were conducted using a YLR-100 laser system (IPG Photonics, USA) which generated a central wavelength of 1060 nm. The laser beam was scanned across the top surface of the PDMS sheet using a Focus Shifter digital galvanometer laser scanner system (Raylase GmbH, Germany). For the spot experiments, the laser beam was not scanned (i.e., stationary) and the time that laser beam was turned on was externally controlled digitally.

Pulsed laser irradiation experiments were conducted using a Solstice Ace laser system (Spectra Physics, USA) which generated 100-fs laser pulses with a central wavelength of 800 nm at a repetition rate of 1 kHz. Laser pulses were focused onto the top surface of the PDMS sheet using a 10x objective lens, with a numerical aperture of 0.25. Pulse energy was set to be 20 μJ, and was kept constant for all pulsed-laser-related experiments. The PDMS sheet was placed onto a Z-Lift & Vertical Motion stage (ALIO, USA) to scan laser pulses onto the surface.

Both outputted laser beams were axisymmetric and possessed a typical gaussian distribution. All irradiation experiments were conducted in ambient conditions.

2.3. Characterisations

Optical microscopy (OM) and confocal laser scanning microscopy (CLSM) intensity images were obtained using an LEXT confocal laser scanning microscope (Olympus, Japan). Raman spectra were obtained using a LabRAM Aramis laser-excited Raman spectrometer (Horiba, Japan). The excitation wavelength and laser power for Raman analyses were set to 532 nm and approximately 36 mW, respectively. A wave-number range of 400–3200 cm⁻¹ was selected to obtain individual Raman spectra. A wave-number range of 2800–3000 cm⁻¹ was selected to obtain Raman intensity maps. SEM images were obtained using an Inspet F50 scanning electron microscope (FEI, USA). Prior to SEM observations, iridium coatings with a thickness of approximately 10 nm were applied by ion sputtering.

2.4. Temperature simulations

The increase in surface temperature of a PDMS sheet when irradiated by a stationary CW laser beam with a constant laser power was simulated using a 2D axisymmetric finite element model in COMSOL Multiphysics software™ (version 5.5). The default Heat Transfer in Solids module was used for the simulations, and the initial temperature was set at 293 K. The laser heat input (Q) was expressed as a function of r and z by Eq. (1) as [32],

\[
Q(r, z) = P \frac{A}{2\pi R^2} \left(1 - \frac{z}{R} \right)^2 \times e^{-\frac{r^2}{2\sigma^2}}
\]

where P is the laser power, R is the focal beam radius, and A is the absorption coefficient of PDMS for a specific laser wavelength. The top surface of the PDMS sheet was set to be z = 0. The laser beam was irradiated at coordinates of (0,0). The simulated temperatures at (0,0) were recorded for different resident times. The material properties were

\[
\begin{align*}
\text{Discontinuous} \quad \text{[X]} \\
\text{Continuous} \quad \text{[O]} \\
\end{align*}
\]

Fig. 1. Respective OM and CLSM intensity images of structures formed with (a and d) 720 mm/s, (b and e) 480 mm/s, and (c and f) 240 mm/s, with a constant laser power of 80 W. g Structural formation for different laser power (P) and scanning speed (v) combinations. Discontinuous and continuous combinations are indicated by red crosses and blue circle markers, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

\[
\begin{align*}
\text{Discontinuous} \quad \text{[X]} \\
\text{Continuous} \quad \text{[O]} \\
\end{align*}
\]
assumed to be constant throughout the simulations, as the simulations at this time were focused on understanding the initial growth mechanics of defects (before considerable material conversion). To calculate the induced temperatures after $t_{\text{critical}}$ with more accuracy, the dynamic change in material properties should to be considered; however, are out of the scope of the current study. Supplementary Table S1 lists the properties, variables, and values used for the simulations.

3. Results and discussions

A CW laser beam was focused and scanned across the surface of a PDMS sheet with different laser powers and scanning speeds to assess which parameter combinations allow for the continuous formation of structures while laser scanning. The parameter combination was defined to be “continuous”, if there is a visibly continuous structure 2 mm or longer in at least 3 out of 5 experiments. Parameter combinations resulting in anything else, including no visible modification, was deemed “discontinuous”. Note that material compositions and properties were disregarded from defining the continuity. Fig. 1a-f shows OM and CLSM intensity images of representative discontinuous and continuous structures with a constant laser power of 80 W. From the OM images (Fig. 1a–c), it can be observed that the surface of the transparent PDMS sheet was modified into a visibly black-colored material after laser scanning. For a scanning speed of 720 mm/s (Fig. 1a), 480 mm/s (Fig. 1b), and 240 mm/s (Fig. 1c), the formation of defects, islands, and a track is observed, respectively. From the CLSM intensity images (Fig. 1d–f), especially those of defects (Fig. 1d), it is clearly shown that the black-colored structures are 3D and slightly protruding from the surface. It has been discussed in the case of the laser ablation of polymers that due to air-polymer surface boundary effects, such as light scattering and/or thermal conduction, maximum temperatures are induced a few μm below the surface [12,33,34]. As the polymer decomposes, a bubble filled with gaseous products will form below the surface. With continued laser irradiation, the bubble will expand, and eventually explode through the polymer surface, resulting in a protruding defect [34].

![Fig. 2. OM images of defects formed with resident times of $t = a$ 0 μs, $b$ 90 μs, $c$ 166 μs, $d$ 250 μs, and $e$ 500 μs, with a constant laser power of 40 W. Black asterisks indicate the $t_{\text{critical}}$ for each laser power. f Experimentally measured diameters (d) of defects formed with different laser powers and resident times (t). Dashed lines indicate the peak temperatures (T) with respect to resident time simulated with COMSOL for different laser powers. Inset shows the measured diameters of defects for resident times greater than $t_{\text{critical}}$ with respect to $t^{1/2}$.](image)

The type of structure formed for each laser power (P) and scanning speed (v) parameter combination is summarized in Fig. 1g. Parameter combinations resulting in a visibly continuous track is indicated with a blue circle, whereas parameter combinations resulting in anything else is indicated with a red x-mark. It is observed that the scanning speed required for the continuous formation of tracks tends to increase as the laser power is increased. However, it can be observed that the parameter combinations which yield continuous formation cannot be determined solely from the laser irradiance (I), which can be expressed by Eq. (2) as [35],

$$I = \frac{P}{v2R}$$  \hspace{1cm} (2)

where R is the focal beam radius of the laser beam fixed at 50 μm in this study. With the same laser irradiance, continuous tracks were able to be formed with low laser power and slow scanning speed parameter combinations, whereas tracks could not be formed with high laser power and fast scanning speed parameter combinations. The results of Fig. 1g clearly indicates that the resulting structure does not strictly depend on the combined parameter of laser irradiance but rather on the scanning speed.

Considering a unit distance of the PDMS surface, the scanning speed will be related to the resident time of the laser beam. To shed some light...
on the effect of resident time on the structure formation, a stationary laser beam was irradiated onto the surface of a PDMS sheet and the resident time was changed. Fig. 2a–e shows OM images of structures formed with different resident times (t) with a constant laser power of 40 W. At 90 μs, the formation of a defect smaller than the focal beam diameter (50 μm), with a polymeric flap (location marked as A), is observed on the surface (Fig. 2b). As the resident time is increased, the defect grows in diameter (Fig. 2c), and the formation of evident bubble-like bumps are observed on the defect surface (location marked as B) (Fig. 2d and e). Moreover, the surfaces neighboring the defects (Fig. 2b–e) were considerably contaminated compared to before laser irradiation (Fig. 2a), possibly due to the ejection of debris during explosive formation (location marked as C). These observations are consistent with the below-surface explosive mechanism for defect formation discussed earlier. The filled circles in Fig. 2f shows the experimentally measured diameters (d) of the defects formed at different resident times (t) with various laser powers. For all laser powers, the defects significantly grew in diameters at a critical resident time, $t_{\text{critical}}$ (indicated by the black asterisks in Fig. 2f). Moreover, the increase in diameter after $t_{\text{critical}}$ was linearly related to $t^{1/2}$ (inset Fig. 2f). This is expected, as defect growth beyond the focal beam diameter is driven by radial diffusion of thermal energy, and should correspond to the thermal diffusion length ($l$), which is approximated with Eq. (3) as,

$$l = \frac{d}{2} = \sqrt{4\alpha t}$$

where $\alpha$ is the thermal diffusivity of the material. From the results shown in the inset of Fig. 2f, $\alpha$ can be calculated to be approximately 0.9 cm$^2$/s, which agrees with the thermal diffusivity of pristine PDMS which is approximately 1.1 cm$^2$/s.

Since the growth mechanics of the defects are closely related with thermal effects [36], the time-dependent temperature change in the PDMS surface resulting from the irradiation of a stationary laser beam with a constant laser power was simulated using COMSOL. The properties of the target material, in this case PDMS, were assumed to be constant throughout the simulations. The details regarding the simulations are given in the Experimental section. The increase in peak temperature with respect to resident time for each laser power is plotted in Fig. 2f as dashed lines. PDMS starts decomposing at a temperature of approximately 600 K, and starts graphitizing into crystallites of graphitic carbon within a temperature range of 1100–1300 K [37]. Accordingly, $t_{\text{critical}}$ coincides with the critical translation time in which the temperature shifts from the decomposition temperature (indicated as the orange region) to the graphitization temperature (indicated as the blue region). In other words, the defects significantly grow in size when the temperature induced by laser irradiation reaches the temperature threshold for graphitization. As graphitic carbon forms, the properties of the irradiated material, specifically the absorption coefficient, increases substantially from approximately 3 cm$^{-1}$ for pristine PDMS [38] to 40000 cm$^{-1}$ for graphite [39]. This will result in a drastic increase in the absorbed laser energy, and a sudden increase in defect size.

To investigate if the COMSOL temperature simulations align with the actual resulting material due to laser irradiation, material analyses were conducted on the defects. Fig. 3a shows Raman spectra obtained from the defects formed at different resident times with a constant laser power of 40 W. The Raman peaks and their originating bonds for pristine PDMS are listed in Supplementary Table S2. Note that each spectrum was normalized with respect to its individual raw maximum intensity value. For resident times of 200 μs and 250 μs, only PDMS-related peaks are confirmed, indicating no significant alteration in chemical structure. At a resident time of 200 μs, the emergence extremely weak peaks are observed at 1350 cm$^{-1}$ and 1580 cm$^{-1}$. Such peaks are commonly referred to as the D and G bands and originate from out-plane vibrational modes of defects and edge functional groups of sp$^2$-hybridized carbon domains, and in-plane vibrational modes of sp$^2$-hybridized carbon domains, respectively [40]. For resident times of 200 μs and 250 μs, a significant increase in the relative intensities of the D and G bands, as well as the emergence of broad peaks at 860 cm$^{-1}$ and 2700 cm$^{-1}$ are observed. The 860 cm$^{-1}$ peak originates from vibration modes of silicon carbide (SiC) nanocrystals [41], and is consistent of previous reports indicating the formation of SiC nanocrystals by the laser irradiation of PDMS [30,31]. The fact that sharp transverse optical and longitudinal optical vibration modes of SiC cannot be distinguished indicates that the formed SiC nanocrystals are extremely small or highly defective [41]. The 2700 cm$^{-1}$ peak is commonly referred to as the G’ band, and originates from the second-order resonance modes of sp$^2$-hybridized carbon domains [42]. The emergence of the broad symmetrical G’ band suggests that the graphitic carbon is multilayered and turbostratic in orientation [43,44].
The emergence of the strong D and G bands, in addition to the G band, after resident times of 200 μs and longer is consistent with the COMSOL results suggesting the transition into the graphitization temperature.

Fig. 3b shows the relative intensities of the m band (Im) and the G band (IG) for each resident time. The Im and IG values for each resident time were normalized with respect to the raw Im and IG values for a resident time of 90 μs. Although significant differences in the shape of the spectra could not be distinguished for resident times shorter than 166 μs, a gradual decrease in Im is observed with an increase in resident time, suggesting progressive dehydration of the methyl groups by laser irradiation and the decomposition of PDMS. As the resident time is further increased to 250 μs, Im continues to decrease to less than 1 % of the initial intensity at 90 μs. Contrarily, an increase in the IG is observed with the increase in resident time. For resident times of 143 μs and 166 μs, slight increases in relative IG are observed. Considering the extremely weak intensity, this is indicative of the formation of amorphous carbon domains within a polymeric matrix rather than formation of distinct crystalline graphitic domains [37,44,45].

For resident times of 200 μs and 250 μs, a comparably higher IG is observed, indicating the formation of larger distinguished graphitic domains. The critical time in which significant transformation in material composition to graphitic carbon occurs, suggested by the large change in IG, matches well with t_{critical} for the significant growth of defects (Fig. 2b and Supplementary Fig. S1).

Table 1 summarizes the times where growths of defects were observed in Fig. 2f (t_{critical}), scanning speeds where shifts from discontinuous to continuous structures were observed in Fig. 1b (v_{continuity}), and assumed resident times calculated from v_{continuity} (t_{continuity}) for each laser power. In the case of laser powers of 80 W, 60 W, and 40 W, t_{critical} matches well with t_{continuity}, and suggests that continuous track formation occurs when the temperature reaches that for the initiation of graphitization. However, in the case of a laser power of 20 W, t_{critical} is significantly longer than t_{continuity}, suggesting temperature lower than the graphitization temperature are sufficient for continuous track formation.

A formation mechanism which explains the difference in resident times required for continuous track formation is proposed in Fig. 4. Laser scanning of the PDMS surface will induce a localized increase in temperature, in which the peak temperature should depend on the laser irradiance. Considering the same laser irradiance, low laser powers and slow scanning speed parameter combinations will induce slower heating of the PDMS sheet compared to high laser power and fast scanning speeds parameter combinations. As the PDMS sheet is heated to the decomposition temperature and with sufficient time, the formation of bubbles below the surface will initiate the nucleation of a protruding defect (Phase 1). Such defects will be scattered as nucleation is homogeneous [46]. In the case of slow heating (Fig. 4a1), as there is an abundant time for the nucleation of laser-induced defects, the overall number of defects will be greater than in the case of fast heating (Fig. 4b1). As the PDMS sheet is further heated, the preexisting defects will act as initiation sites and slightly grow in size. Moreover, the number of defects will steadily increase due to additional nucleation. As the defects come into contact with neighboring defects, they will merge to form larger structures (Phase 2). In the case of slow heating, since the density of defects is high, merging of neighboring defects will result in a continuous track (Fig. 4a2). On the contrary, in the case of fast heating, since the density of defects is low, merging of neighboring defects will only result in discontinuous islands (Fig. 4b2), as observed in Fig. 3b. Once the temperature reaches the graphitization threshold, the defects will significantly grow in size, further bridging neighboring unmerged structures (Phase 3). Unlike the case of slow heating, in the case of fast heating the exponential growth in defect size owing to graphitization is required to compensate for the low defect density in order to achieve continuous tracks (Fig. 4b3). As a result of the differences in defect densities, the resulting graphitic track in Phase 3 is expected to be more uniform and denser in the case of slow heating (Fig. 4a3) compared to fast heating (Fig. 4b3).

To validate the proposed formation mechanism, structures formed by relatively slow heating and fast heating were compared. Material analyses preformed on structures formed with assumed temperatures in the decomposition temperature (low laser irradiance), are shown in Fig. 5a-c. For 20 W, 200 mm/s (slow heating), the formation of a significant number of defects is observed (Fig. 5a). For 20 W, 400 mm/s (fast heating), the formation of a significant number of defects is observed (Fig. 5b). For 40 W, 200 mm/s (slow heating), the formation of a significant number of defects is observed (Fig. 5c). For 40 W, 400 mm/s (fast heating), the formation of a significant number of defects is observed (Fig. 5d).

Table 1

<table>
<thead>
<tr>
<th>P (W)</th>
<th>t_{critical} (μs)</th>
<th>v_{continuity} (mm/s)</th>
<th>t_{continuity} (μs)</th>
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<tbody>
<tr>
<td>20</td>
<td>100-111</td>
<td>480-400</td>
<td>104-125</td>
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<tr>
<td>60</td>
<td>125-142</td>
<td>420-360</td>
<td>119-139</td>
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<tr>
<td>40</td>
<td>166-200</td>
<td>320-280</td>
<td>156-179</td>
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<tr>
<td>20</td>
<td>250-333</td>
<td>260-240</td>
<td>192-208</td>
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Fig. 4. Schematic of the proposed formation mechanism of continuous tracks in the case of a slow and b fast heating by laser irradiation. Subscripts correspond to the respective phases.
A continuous track can be observed (Fig. 5a). On the other hand, for 80 W, 800 mm/s (fast heating), the formation of discontinuous defects can be observed (Fig. 5b). However, comparing the Raman spectra obtained from the structures, it is revealed that the material compositions of the track and defects are comparable (Fig. 5c). Moreover, the relatively weak G band peak and high \( I_m \) supports the assumption that the induced temperatures are in the decomposition temperature [44]. These results clearly support the differences in Phase 2 between slow and fast heating illustrated in Fig. 4a2 and b2, respectively.

Next, material analyses performed on structures formed with assumed temperatures in the graphitization temperature (high laser irradiance), are shown in Fig. 5d–k. Compared to the structures in Fig. 5a, all structures are visibly continuous regardless of parameter combinations (Fig. 5d–g). For 20 W, 80 mm/s (slow heating), the entirety of the track appears black colored (Fig. 5d). However, as the laser power and scanning speed increase (shift towards faster heating), non-black-colored regions start to emerge (Fig. 5e–g). Moreover, for 80 W, 320 mm/s (Fig. 5g), the black-colored regions are distributed in patches (red circles). Fig. 5h–k shows Raman intensity maps with regards to \( I_m \) for a 72 \( \mu \)m \( \times \) 72 \( \mu \)m area. The bright regions represent a high \( I_m \), indicating a low degree of graphitization, whereas dark regions represent a low \( I_m \), suggesting a high degree of graphitization (Supplementary Fig. S2). For the Raman intensity map of 20 W, 80 mm/s (Fig. 5h), the whole field-of-view is dark, suggesting high degree of graphitization of the entire area. As the laser power and scanning speed increase (Fig. 5i–k), bright regions start to emerge. The bright regions observed in the Raman intensity maps corresponded to the non-black-colored boundaries observed in the OM images. For the Raman intensity map of 80 W, 320 mm/s (Fig. 5k), dark regions, or graphitic structures, are observed as dark patches (yellow arrows), consistent with OM observations (Fig. 5g). These results clearly support this difference in Phase 3 between slow and fast heating mentioned in Fig. 4a2 and b2, respectively.

Thus far, it has been discussed that the continuous tracks are a result of the merging of smaller defects. In other words, even with parameter combinations that result in discontinuous structures (Fig. 5a, top inset), continuous tracks should be obtainable by increasing the defect density via multiple laser scans. By forming defects with the first scan, such defects can function as initiation sites for the second scan, and the formation process can start at Phase 2 of the proposed model (Fig. 4). Fig. 6a–c shows OM images of structures formed with multiple scans for a constant parameter combination of 80 W, 800 mm/s. With 1 scan (Fig. 6a), the formation of scattered defects can be observed. As the number of scans increase (Fig. 6b and c), a gradual growth of structure into a continuous track can be observed. The multi-parameter orthogonal experiment was repeated with multiple scans, and the type of structure formed for each parameter combination is summarized in Fig. 6d. As the number of scans increase, the parameter combinations
Fig. 6. OM images of structures formed with a 1, b 2, and c 3 laser scans, for a constant parameter combination of 80 W, 800 mm/s. d Structural formation for different laser power (P) and scanning speed (v) combinations, with different number of laser scans. Discontinuous and continuous combinations are indicated by red crosses and blue circle markers, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Schematic of the two-laser LDW technique in which a first, fs laser pulses are scanned to mark the surface with defects, b then, a CW laser beam is traced to form a continuous track along the defects. c SEM image of an array of defects formed by raster scanning of fs laser pulses. OM images of structures formed by CW-LDW with defect spacings (s) and scanning speeds of d 20 μm, 800 mm/s, e 40 μm, 800 mm/s, f 60 μm, 800 mm/s, g 20 μm, 960 mm/s, h 20 μm, 960 mm/s, and i 20 μm, 1200 mm/s, for a constant laser power of 80 W.
which yield continuous formation increases, particularly for higher laser powers and faster scanning speeds. Moreover, in the case of multiple scans, it can be observed that the parameter combinations which yield continuous formation can be determined from laser irradiance. The results thus far clearly indicates that the processing speed limit for the formation of continuous tracks is restrained due to the time required for the nucleation and growth of laser-induced defects.

In order to further validate the importance of defects on the formation of continuous tracks, defects were intentionally introduced to the PDMS surface by simply irradiating focused femtosecond (fs) laser pulses into a pristine PDMS surface (Fig. 7a), prior to the scanning of a CW laser beam (Fig. 7b). Fig. 7c shows a SEM image of an array of defects marked on the surface of a PDMS sheet via fs LDW. Formation of graphitic carbon was not confirmed from the irradiation of fs laser pulses alone (Supplementary Fig. S5). Moreover, the surfaces of the defects formed by the irradiation of fs laser pulses were significantly smoother than those formed by the irradiation of a CW laser beam (Supplementary Fig. S3 and S4), suggesting the formation of fs-LDW defects were a result of laser ablation owing to the high laser intensity [47]. Although a continuous track could not be formed with a parameter combination of 80 W, 800 mm/s in the case of an un-marked PDMS surface (Fig. 1g), a continuous carbon track was successfully formed along the defects in the case of the marked PDMS surface (Fig. 7d, e, and Supplementary Fig. S5). Note that continuous tracks could only be formed when the spacing between the defects (s) was sufficiently close (Fig. 7f). Furthermore, the defect spacing required for continuous track formation decreased with an increase in scanning speed of the CW laser beam (Fig. 7g–i). This is expected as the increase in scanning speed will decrease the laser irradiance, resulting in smaller growths of the defects. It should be noted that the reproducibility of the continuous-track formation was also significantly improved in the case of the marked surface. Although the exact reason for the fs-LDW defects assisting the formation of continuous carbon tracks cannot be concluded at this time, it can be attributed to a decrease in formation threshold (e.g., increase in optical absorbance) due to alternations in the surface chemical composition. In the case where only a CW laser system is used, the viable processing speeds for continuous track formation is significantly limited due to temporal requirements for defect nucleation. On the other hand, as the mechanism for defect nucleation is different between the irradiation of a CW laser beam (i.e., evaporation and bubble growth) and a fs laser pulse (i.e., surface ablation), fs laser processing will have less of a temporal limitation due to defect nucleation. Therefore, by developing a two-laser LDW technique, which incorporates a fs laser system for defect nucleation and a CW laser system for thermal growth and graphitization, the current processing limits, such as processing speed and reproducibility, can be overcome with regards to the patterning of continuous carbon tracks on flexible transparent polymers.

4. Conclusions

In this study, we proposed a formation mechanism of 3D carbon tracks on polymers by laser irradiation based on the formation and growth of laser-induced defects. Our proposed formation mechanism is composed of 3 phases, (1) nucleation of laser-induced defect, (2) slow growth of defects and increase in defect number, and (3) the sudden growth of defects due to graphitization. Depending on if the laser parameter combinations lead to slow heating or fast heating, the specifics of these 3 phases will change drastically, resulting in noticeably different structures even with the same laser irradiance. Orthogonal multi-parameter experiments for single laser scans indicated that the structure formation is not solely dependent on the laser irradiance but rather on the resident time of the laser beam, limiting the processing speeds for the LDW of 3D carbon structures. Orthogonal multi-parameter experiments for multiple laser scans suggested that the temporal limitation is due to the time required for the nucleation and growth of defects. Based on this, defects are intentionally introduced in a controlled manner to further validate formation mechanism based on laser-induced defects. In the future, by designing an optical setup in which both fs and CW laser systems are incorporated into the same beam path, the ultrafast and single-stepped LDW of 3D carbon tracks can be achieved. The insights shown in this study will provide the necessary developments of the 3D carbon-LDW technique to transition towards a viable manufacturing process of the roll-to-roll functionalization of flexible and transparent polymer substrates for the production of various novel devices, namely wearable electronics and optical sensing elements. Moreover, although this current study was focused on understanding the underlying mechanisms for structure formation regarding the laser-induced graphitization of polymers, the idea of laser-induced defects for structural formation may provide an important foundation to understand the structural formation mechanism for other materials and LDW techniques.

CRediT authorship contribution statement

Shuichiro Hayashi: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. Xiaohan Du: Writing – review & editing, Methodology, Formal analysis. Marco Rupp: Writing – review & editing, Methodology, Investigation. Kai A. Filsinger: Writing – review & editing, Methodology. Mitsuhiro Terakawa: Writing – review & editing, Supervision, Conceptualization. Craig B. Arnold: Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary material to this article can be found online at https://doi.org/10.1016/j.optlastec.2024.110686.

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