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Ultrafast Laser Direct Writing of Conductive Patterns on Polyimide Substrate

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ABSTRACT

Laser direct writing (LDW) is a fast and cost-effective method for printing conductive patterns in flexible polymer substrates. The electrical, chemical, and mechanical properties of polyimide (PI) make it an attractive material choice for laser writing of conductive circuits in such polymer. Electrically insulating PI has shown great potential for flexible printed electronics as LDW enables selective carbonization in the bulk of such material leading to the formation of conductive lines. However, existing studies in this area reveal a few key limitations of this approach including limited conductivity of written structures and fragility of carbonized PI. Therefore, more research is required to overcome those limitations and reap the benefits of the LDW approach in writing flexible electronic circuits in PI. The proposed study investigates potential approaches to enhance the electrical conductivity of femtosecond laser written bulk carbon structures in PI films. Deposition of laser energy was varied by changing key process parameters such as pulse energy, pulse picker divider, and hatch distance of laser scan to maximize the conductively of the carbon structure. The experimental findings show a strong dependency of laser energy deposition on the conductivity carbon structures in PI films. To further enhance the electrical conductivity of laser written structures, the feasibility of adding copper microparticles to the PI solution and subsequent laser carbonization was studied. The proposed LDW of conductive lines has potential in flexible electronic circuits and sensing applications.

Keywords: Polyimide, Laser direct writing, Ultrafast Laser System, Pyrolysis, Carbonization, Printed electronics.

1. INTRODUCTION

Flexible electronics on large-area polymeric substrates is a rapidly growing technology with a diverse number of applications. In the high-tech domains like electrical insulation, electronic packaging, sensor, medical sector, and aerospace, aromatic polyimide films have been widely in a variety of forms, including film, fiber, nanofiber, membrane, foam, adhesive, and coating due to its excellent balance of thermal, mechanical, and electrical properties [1,2]. The method of laser-induced carbonization has been investigated for converting polyimide into a porous carbon material suitable for usage in devices; for example flexible electronics and sensors [3,4]. The revelation that laser radiation increases the conductivity of polymer surfaces is significant for prospective applications in the microelectronics industry. For the patterning of carbon microelectrodes, laser pyrolysis has been proposed as a new approach [4,5]. Under ultraviolet laser irradiation, the electrical conductivity of PI can increase by 15 to 16 orders of magnitude [3,6]. The irradiated sites are mostly made up of C-C bonds [7]. The basic mechanism for laser pyrolysis is photothermal carbonization caused by laser irradiation. The photonic energy is transformed into heat when photons are absorbed by the polymer. The laser beam has a high intensity, and the polymer has a low heat conductivity, resulting in a big temperature gradient in a small zone [8,9]. This process is very fast, and the heating is concentrated in a precise area. Thus, microscale carbon patterning is enabled by scanning a polymer film with a laser beam, while the unaffected polymer area remains intact [8,10]. The temperature threshold is nearly 850ºC for driving the synthesis of graphitic carbon [11].

Laser irradiation of a PI surface can significantly progress its electrical conductivity, there is still a lot of space for enhancement when it comes to developing electrodes. For appropriate laser-induced carbonization, the photo-thermal and photodegradation mechanisms have been thoroughly explored by researchers. To attain induced conductivity, the laser irradiation factors for the construction of carbon structure in polyimide surface must be well tailored for real life application. Initially, the effect of deposited laser energy, pulse picker divider and scanning speed on the conductivity of LDW produced conductive circuits were investigated in this paper. Different laser powers and scanning speeds were first tested, and then an optimum set of laser energy and scanning speed was employed in the experiment. The polyimide film was then altered to create a PI-Cu composite film in order to explore its effects on conductivity.

2. MATERIALS AND METHODS

2.1 Material preparation

The fully imidized polyimide resins in granulate form (TECAPOWDER P84, SG, inventory# 58698-66-1) from Engineer Sintimid GmbH, Austria were dissolved in the dipolar aprotic solvent, 1-Methyl-2-pyrrolidinone (NMP) to create thin PI films. 22 wt.% of polyimide resins were dissolved in NMP solvent for 24 hours on a mixer at low speed. Figure 1 shows the PI in liquid form after 24 hours of mixing. To make the film from the solution dip-coating procedure was used and then cured at room temperature according to specification sheet. The dip-coated PI films were dried in laboratory conditions to prepare the fully cured PI substrates. Digital calipers were used to measure the thickness of the prepared PI film, which was around 250-300μm.

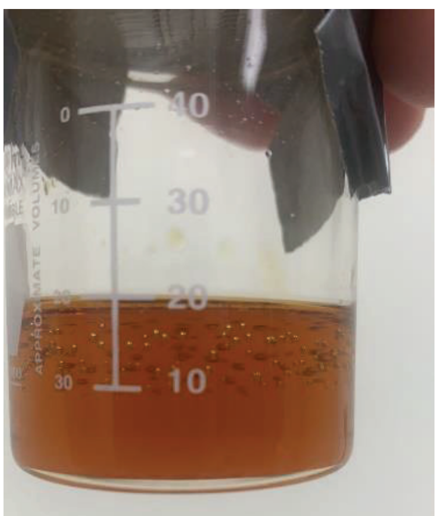

FIGURE 1: LIQUID PI PREPARED FROM 22 WT.% OF POLYMER RESIN DISSOLVED IN NMP.

To improve the conductivity of laser carbonized lines on PI substrate, a feasibility study was conducted by mixing copper (Cu) micro-particle. Primarily, the PI-Cu composite was created by mixing 10 wt.% of Cu micro-particles (copper powder, spherical, APS 10 micron, 99.9% trace metals basis from Beantown Chemical) in the polyimide solution.

2.2 Ultra-fast laser carbonization

A commercially available ultrafast pulsed Nd:YAG laser (a Spirit® laser from Spectra-Physics), operating at a center wavelength of 1040 nm, pulse duration of 500 fs, and maximum pulse energy of 40 μJ at 200 kHz was used to perform the experiments. With an integrated acousto-optic-modulator, the basic repetition rate can be divided by an integer value. Spirit® provides laser parameter optimization for femtosecond lasers used in high-precision manufacturing of polymers, thin metals, and a variety of other materials.

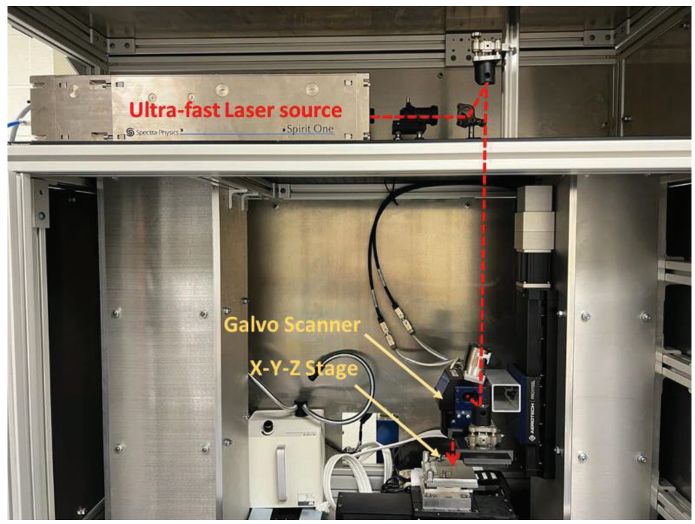

FIGURE 2: THE ULTRA-FAST LASER SYSTEM USED FOR CARBONIZING PI SUBSTRATES.

Ultrafast laser radiation was employed to selectively carbonize PI film to alter its electrical property. To carbonize the polyimide film the laser beam should deliver the threshold energy required to initiate the pyrolysis process, which can be accomplished at different laser energies and scanning speeds. Initially, different laser energy and scanning speed was tested. Excess thermal energies result in cutting through the substrate or damage the substrate while low thermal energies will be unable to carbonize the polymer effectively. All the tests were conducted using a laser energy of 3μJ and a scanning speed of 10mm/s, which had significant effects on the carbonization of PI. To optimize the outcomes, the hatch distance of the scanned lines was varied. Hatch distances of 25μm, 50μm, and 75μm were tested, where the laser beam spot size was 30μm. The basic pulse repetition rate was varied selecting different pulse picker divider (PPD). The PPDs of 1, 2, 3, and 4 were considered to alter the total laser energy deposition onto the PI substrates for printing conductive paths. Straight lines were scanned by laser irradiation on polyimide and all the conductive patterns were 5mm in length with 1mm in width. The morphologies of the conductive lines on PI substrate were investigated using an optical microscope and a scanning electron microscope (SEM) and the resistance were measured using a two prob source-meter from Keithley. The resistance of each conductive path was measured three times.

3. RESULTS AND DISCUSSION

Figure 3 shows the laser carbonized conductive lines on the PI substrates. A pulse picker divider (PPD) was used to control the laser energy deposition in the PI substrates. When lower PPD values such as 1 or 2 were used, dominant carbonization was observed as shown in Fig. 3 (a). For higher values of PPD, fewer pulses were allowed to reach the PI substrate, thus reducing the amount of laser energy into the substrate. Hence, the laser carbonization was less prevalent as carbonized lines appeared lighter in color shown in Fig. 3 (b).

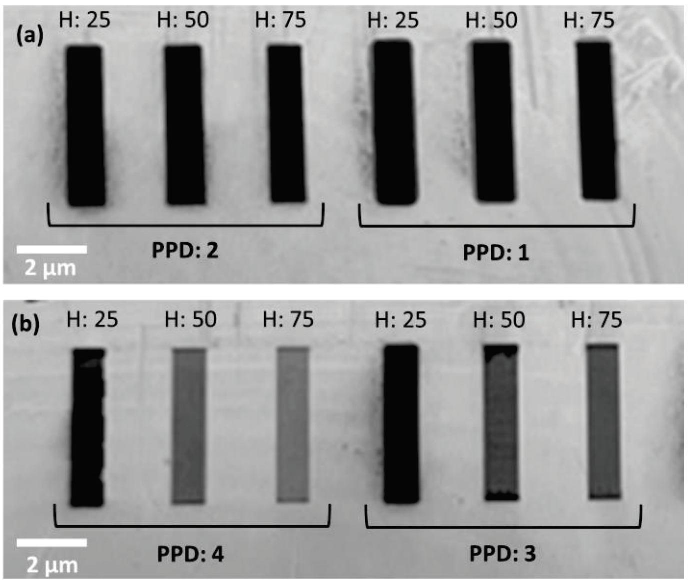

FIGURE 3: IMAGE OF CARBONIZED POLYIMIDE LINES OF DIFFERENT HATCH DISTANCES AND VARYING PPD.

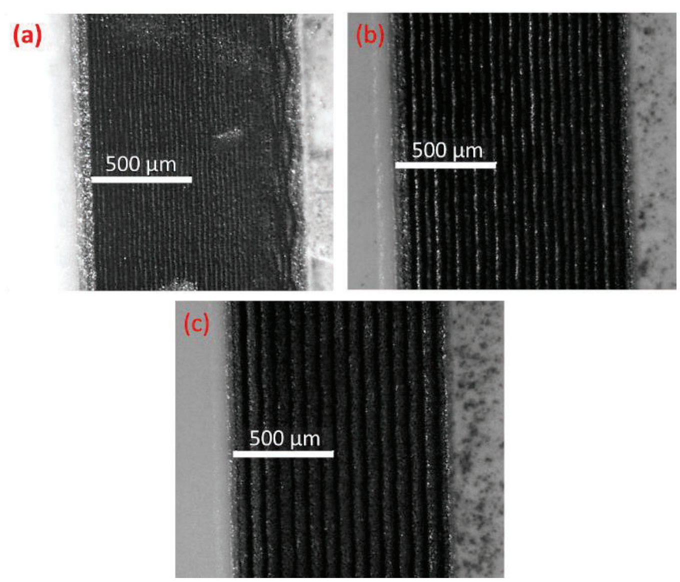

FIGURE 4: MAGNIFIED OPTICAL MICROSCOPE IMAGE OF CARBONIZED CONDUCTIVE PATHS WITH HATCH DISTANCE OF (a) 25 µm, (b) 50 µm AND (c) 75 µm, RESPECTIVELY WITH PPD OF 1.

As shown in Fig. 3, in addition to variable PPD, three different hatch distances of laser scanning were used to control the delivery of laser energy into the PI substrate. For an input pulse energy of 3µJ, the impact of hatch distances of 25 µm, 50 µm, and 75 µm are shown in the optical microscope images of Fig.4 (a), (b), and (c), respectively. Evidence of higher carbonization was observed for lower hatch distance which is also later supported by the lower conduction resistance measured during the testing.

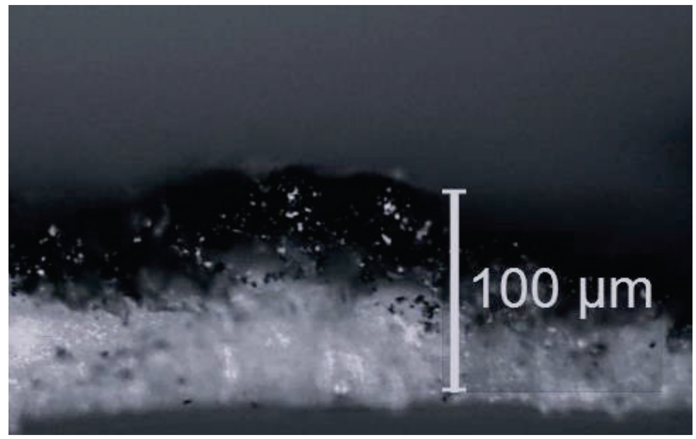

FIGURE 5: A CROSS SECTIONAL MAGNIFIED OPTICAL MICROSCOPE IMAGE OF DEPTH OF THE PYROLIZED PI WITH HATCH DISTANCE OF 25 µm WITH PPD OF 1.

Figure 5 depicts the depth of the pyrolyzed PI. The depth of the carbonized path was between 25-50 µm approximately. Because of the carbonization the film thickness on the that area is reduced.

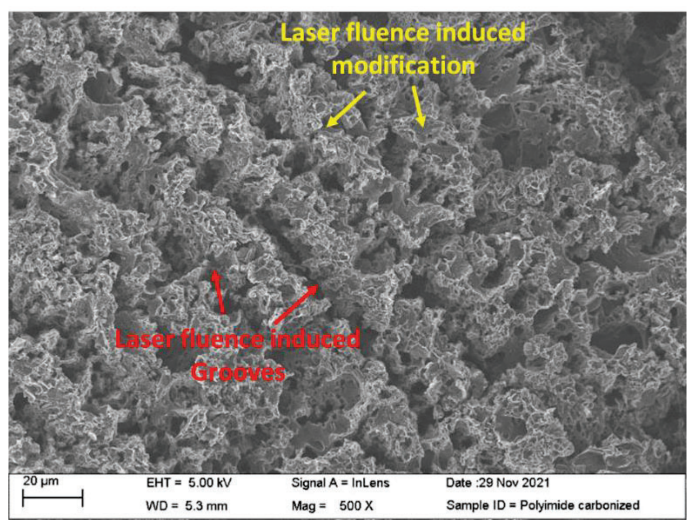

FIGURE 6: SEM IMAGE OF CARBONIZED POLYIMIDE WITH HATCH DISTANCE 25µm AND PPD OF 1.

Figure 6 shows the SEM images of the laser carbonized PI substrate when processed with pulse energy of 3 µJ, PPD of 1, and hatch distance of 25 µm. The grooves are visible along the laser scan paths along with carbonization of PI in between hatches. This explains why the lack of sufficient carbonization in case of larger hatch distance resulted in relatively higher electrical resistance values, as seen in table 1. The energy dispersive X-ray spectroscopy (EDS) shown in Fig. 7 confirms substantial presence of carbon in the laser modified area.

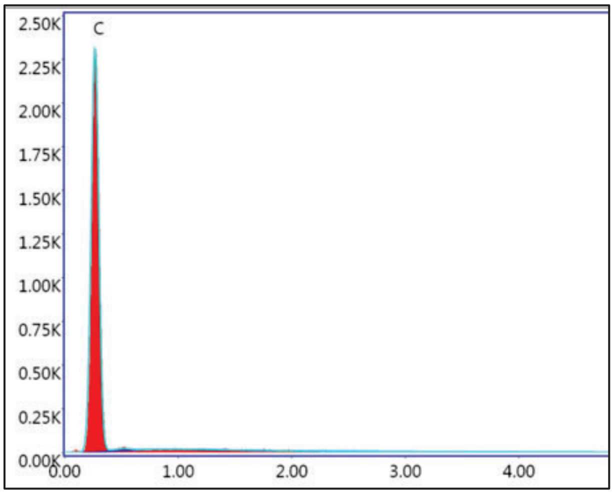

FIGURE 7: EDS GRAPH OF CARBONIZED POLYIMIDE WITH HATCH DISTANCE 25μm AND PPD OF 1.

TABLE 1: A DETAILED STUDY OF THE INFLUENCE OF LASER ENERGY DEPOSITION BY VARYING PPD AND HATCH DISTANCE ON ELECTRICAL PROPERTIES OF THE CARBONIZED LINES.

Hatch (μm)	PPD	Resistance (KΩ) (Three measurement values)
25	1	0.12, 0.117, 0.11
25	2	0.203, 0.25 0.23
25	3	0.56, 0.61, 0.66
25	4	Infinite
50	1	0.15, 0.16, 0.12
50	2	0.38, 0.70, 0.91
50	3	150000, 154000, 160000
50	4	Infinite
75	1	0.33 0.30, 0.36
75	2	1.29, 1.42, 1.36
75	3	199000, 200000, 197800
75	4	Infinite

The results presented in Table 1 provide a better understanding of the laser-induced carbonization of PI films. Clearly, the lower values of both PPD and hatch, the laser carbonized lines showed lower electrical resistances. It is worth noting that for higher values of PPD, the electrical resistance of the laser carbonized lines drastically increased for higher values of hatches. Lack of sufficient carbonization is believed to be the primary reason for such electrical properties. Figure 8 shows the influence of hatch distance on the electrical resistance of carbonized lines on PI substrate for the PPD values of 1 and 2. The results again illustrate an improved electrical conductivity for lower values of both PPD and hatch distance.

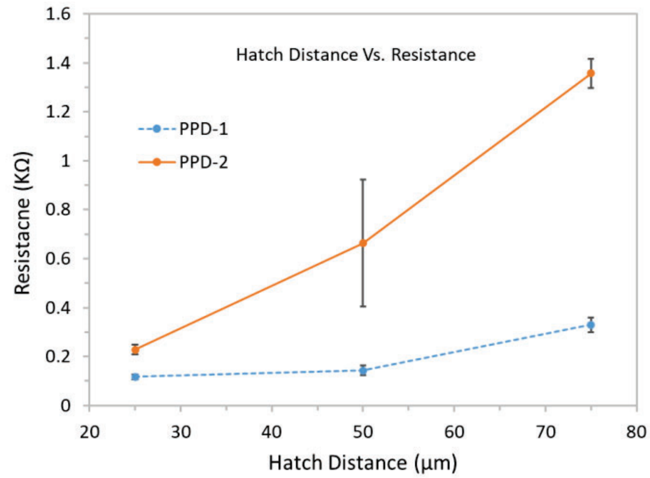

FIGURE 8: GRAPH SHOWING THE INFLUENCE OF HATCH DISTANCE OF LASER SCAN PATH TO RESISTANCE OF THE CARBONIZED CONDUCTIVE PATH.

Laser-induced change in electrical resistance of the PI-Cu composite was also studied, and the initial results did not show any significant improvement in conductivity when PI-Cu was used instead of PI only. The primary results are shown in Table 2 for an input pulse energy of 3 μJ. It is considered that the 10 wt.% micro-particles (max size of 40 μm) in the PI substrate was not enough to contribute to the enhancement of electrical conductivity. The SEM image shown in Fig. 9 shows the random presence of copper micro-particles in the laser carbonized area. The Cu particles appear to be quite far from each other, and such infrequent presence of Cu particles are expected not to contribute significantly enhancing its electrical conductivity. As shown in Fig. 10, the EDS result shows the presence of carbon, copper, oxygen elements when the measurement was taken over the entire window of sample shown in Fig. 9. The presence of oxygen in the sample believed to be the result of oxidation of copper during laser irradiation and environmental impact. Although the presence of Cu particles did not significantly improve electrical conductivity, this study suggests usage of smaller metal particles for better dispersion in the PI substrate.

TABLE 2: RESISTANCE OF THE CONDUCTIVE PATH FOR PI-Cu COMPOSITE FILM.

Hatch (μm)	PPD	Resistance (KΩ)
25	1	0.10
25	2	0.33
50	1	0.73
50	2	120
75	1	0.99
75	2	260

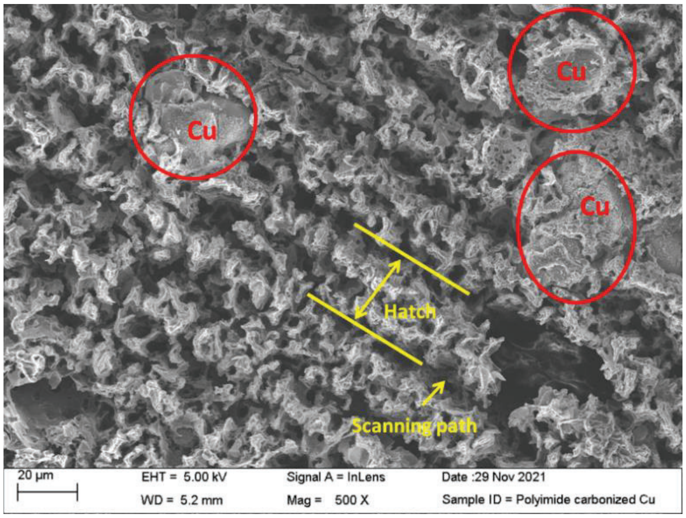

FIGURE 9: SEM IMAGE OF THE CARBONIZED PI-Cu COMPOSITE SUBSTRATE FOR HATCH DISTANCE 25µm AND PPD OF 1.

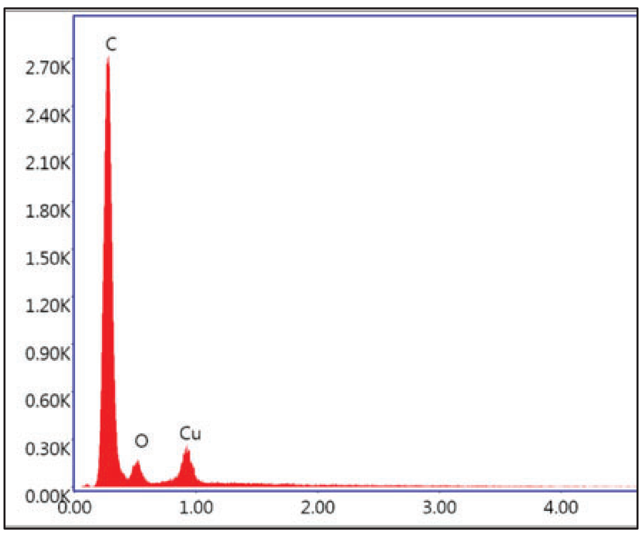

FIGURE 10: EDS GRAPH THE CARBONIZED PI-Cu COMPOSITE SUBSTRATE FOR HATCH DISTANCE 25µm AND PPD OF 1.

The application of higher input laser energy appeared to considerably reduce the electrical resistance of the laser carbonized PI-Cu composite substrate. For example, for an input pulse energy of 8 µJ and hatch distance of 50µm, the resistance of the conductive line was observed to be 30Ω. Carbonization of the PI-Cu film needs to be further looked at to better understand laser-induced electrical resistance change in such composite.

4. CONCLUSION

In summary, we studied ultra-fast laser-induced carbonization of polyamide to selectively enhance electrical conductivity within the PI substrate for printed electronics applications. Controlled deposition of laser energy was found to be the key parameter to enhance the electrical conductivity of the PI substrate. The feasibility of metal micro-particles dispersed in PI was also studied to increase the conductivity of laser carbonized lines. Primary results show great potential for laser-induced conductive circuits for the printed electronics industry.

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