

Eco-Friendly and Rapid Fabrication Method for Producing Polyethylene Terephthalate (PET) Mask Using Intensive Pulsed Light

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An eco-friendly and rapid fabrication method of processing polyethylene terephthalate (PET) films was developed using a laser printer and a xenon flashlight at room temperature under ambient air conditions by imprinting a pattern onto the PET films. A black square pattern was laser-printed onto various thicknesses of PET films and subjected to flashes of different powers. Using black colored patterns and a certain thickness of PET film, the black ink created a void in the PET film in the form of the set pattern. To understand this phenomenon, we measured the light absorbance spectrum of the xenon flashlight using a one-millisecond sampling rate of UV-vis spectrometer. Furthermore, Red-Green-Blue (RGB) compositions of the printed colors, such as yellow, red, green, blue, and black, were extracted using an image color extraction tool. By investigating the degree of light absorbed by the PET film, the absorbance score was defined by combining the percentage of light intensity with the wavelength of the light and the proportion of each color in the RGB compositions. A complex star pattern and a mask for the fabrication of a copper nanoink electrode were created to demonstrate the industry applications of the method.

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1. Introduction

Intensive pulsed light (IPL) techniques have recently drawn considerable attention in the fields of sintering metal nanoparticles, converting graphene oxide to reduced graphene oxide, and crosslinking polymers, due to its ability to discharge high amounts of power in milliseconds using a xenon flash lamp.¹⁻⁶ The IPL technique allows for the chemical and physical properties of materials to be changed at room temperature under ambient atmosphere. In addition, a reaction time of a few milliseconds means that this method is fast and environmental friendly compared to chemical processes and can easily be reproduced.^{7,8} The IPL technique has the potential to not only change material properties, but also it can be used in other applications such as material removal or patterning polymer sheets, for example, polyethylene terephthalate (PET) film.^{9,10}

Conventionally, PET films can be machined using a sharp cutting tool. However, this process produces material waste, has limitations in design, and requires a high maintenance cost. A laser cutting method was developed to overcome the limitations of physical cutting tools.¹¹⁻¹³ It has

been popular due to its minimum material waste, and lack of design limitations and tools. Although the laser method has several advantages, it can only cut materials by following the track of a laser, and it requires high precision in the lateral X-Y stages or galvanometer to make a pattern. Achieving a low-cost, rapid fabrication process without complex stages and high material waste remains challenging.

This challenge may be circumvented by combining IPL, laser printing, and PET film. A xenon flash lamp has a broad wavelength spectrum ranging from 250 nm to 950 nm.^{2,14} The light from the xenon flash lamp increases the temperature of target materials depending on their absorption capacity. In the case of silicon wafer annealing, silicon has a large wavelength absorption capacity, and therefore, the xenon flashlight can increase the temperature of the silicon wafer by more than 1000°C.^{15,16} However, the light is not able to melt the aluminum reflector due to its milliseconds' exposure time.¹⁶ Likewise, in the case of copper nanoparticles on a polymer film, the light increases the temperature of the copper nanoparticles, which have a peak absorption wavelength around 550 nm, to 350°C, while the temperature of polymer substrate surrounding the copper, is only increased to around

150°C.¹⁷ Therefore, polymer substrates may be machined without damage using this phenomenon.

In this study, the processing of PET films using a xenon flashlight were investigated with multicolored laser printed patterns and different thicknesses of films. The colors yellow, red, green, blue, and black were used due to their various light absorption capabilities. The thickness of the polymer films and the power of the flashlight were optimized to determine the proper machining conditions. To the best of our knowledge, this experiment is the first reported where the IPL technique is used for processing patterns on polymeric substrates in milliseconds at room temperature under ambient atmosphere. The resultant PET films were able to be used as a mask to produce conductive copper electrodes.

2. Experimental

2.1 Laser-Printed PET Films and Processing of PET Films using IPL

Various thicknesses of PET films, 12.7, 25.4, 76.2, and 127 μm , were obtained from McMaster-Carr (USA). Square patterns, 0.25 cm by 0.25 cm, were drawn in yellow, red, green, blue, and black on a computer, and then those colored patterns were printed onto different thicknesses of PET films using a commercial color laser printer (Xerox WorkCentre 7556). The 85 to 95 percent of components in printer toner are superfine polyester powder, and the rest of elements are either carbon black or color pigments. The patterns printed on the various thicknesses of polymer film were subjected to a xenon flashlight with either 1200 (only for black colored pattern), 3400 or 4800 W, for an exposure time of 6 milliseconds to find the optimal power settings of the flashlight and thickness of film. The process of exposing the laser-printed PET films to IPL at room temperature in an ambient atmosphere produced voids in the PET matching that of the printed pattern. The schematic of the process is illustrated in Fig. 1(a).

2.2 Characterization and Applications

The absorption wavelength of a xenon flashlight and the reflectance spectrum of yellow, red, green, blue and black colors onto PET film were measured using a UV-vis spectrometer (Ocean Optics, USA), which has a one-millisecond sampling rate. The colors from the printed patterns were investigated using a digital microscope (Dino-Lite, Taiwan) and image color extraction tools (Digital Color Meter, Apple inc.). The results showed that the intensity spans of red (R), green (G), and blue (B) were from 0 to 255. The investigated colors are summarized in Table 1. A PET star-shaped pattern and a PET complex electrode pattern were created to show the uses of the technique in various applications. The complex electrode pattern was used alongside a copper nanoparticle ink to create an electrode that was implemented in an open electronic circuit, which included a battery source and an LED lightbulb. For the copper nanoparticle ink, copper nanoparticles with 100 nm in diameter obtained from Tekna (Quebec, Canada), poly (N-vinylpyrrolidone) (M_w : 40000 g mol⁻¹), diethylene glycol, and formic acid purchased from Sigma-Aldrich were used in quantities of 0.5 g, 0.06 g, 1 ml and 0.75 ml, respectively. The ink was coated on glass slide with the PET complex electrode pattern by doctor-blade

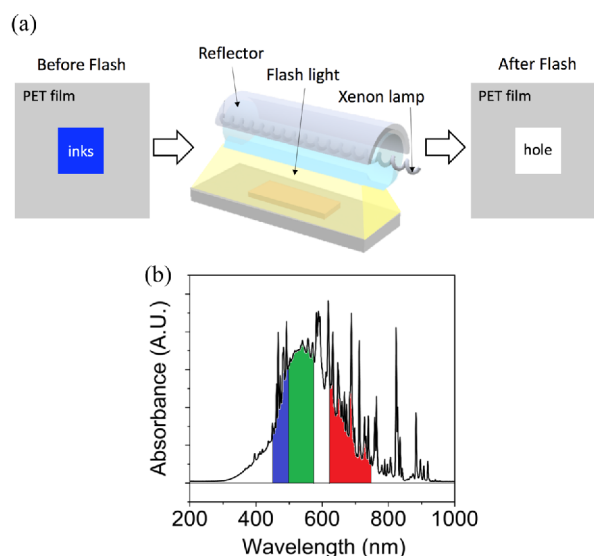


Fig. 1 (a) Schematic illustration of the flashlight system used on a laser-printed PET film before and after flashlight irradiation, (b) UV-Vis spectrum of the light from the xenon lamp. The blue, green, and red colors in the graph indicate the wavelength ranges of each color of light

Table 1 The RGB compositions of the yellow, red, green, blue, and black colors used in the laser-printed patterns on the PET films

Color	RGB composition		
	Red (R)	Green (G)	Blue (B)
Yellow	250	255	2
Red	237	39	5
Green	64	176	80
Blue	59	68	255
Black	0	0	0

method and then dried at 120°C for 15 min to evaporate the solvents. The PET complex electrode pattern was removed before the patterned copper film on glass slide was subjected to xenon flashlight with 4800 W. The details of the copper nanoparticle ink are described elsewhere.²

3. Results and Discussion

Fig. 1(b) shows the wavelength spectrum of the light from a xenon lamp. Under the flashlight, the laser-printed patterns on the PET films absorbed a particular wavelength of light depending on their color, the temperature of the patterned area was increased according to the integrated amount of light. For example, the blue patterns reflected blue wavelengths and absorbed red and green wavelengths, while the black pattern absorbed blue, green, and red light. Further, the blue, green, and red colors in the graph represent the ranges of wavelengths for each color of light.¹⁸ The area percentages of blue (450 nm to 495 nm), green (495 nm to 570 nm), and red (620 nm to 750 nm) from absorbance spectrum of xenon flash light are 12%, 27%, and 24%, respectively. The area of the absorbance spectrum from xenon flash light was calculated using the *trapz* function in MatlabTM. The detailed explanation is demonstrated in Figs. 3 and 4.

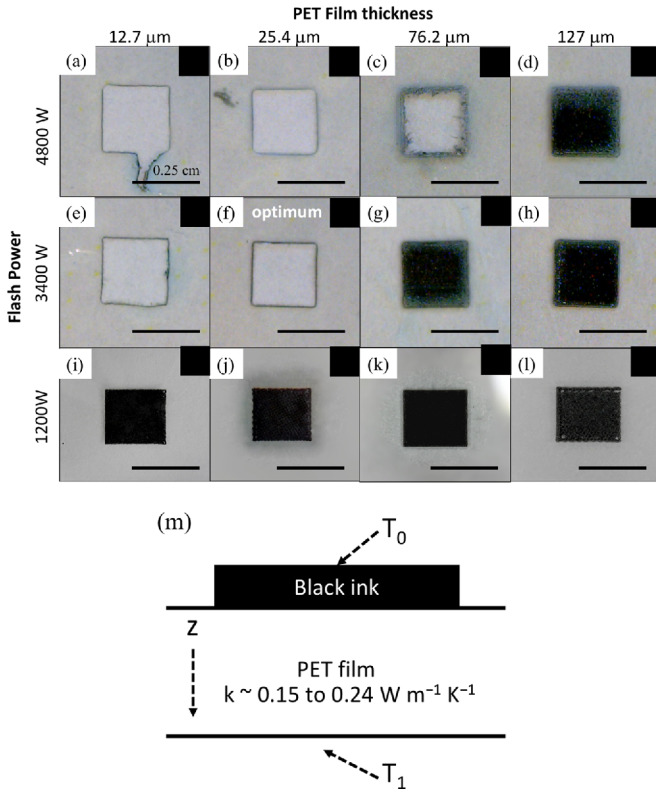


Fig. 2 Optical microscope images of the black square patterned PET films with various thicknesses (a) - (d) after 4800 W, (e) - (h) after 3400 W, (i) - (l) after 1200 W flashlight exposure. (a), (e), (i) 12.7 μm , (b), (f), (j) 25.4 μm , (c), (g), (k) 76.2 μm , (d), (h), (l) 127 μm . The scale bar represents 0.25 cm. (m) Schematic illustration of the side-view of the black ink and PET film

The black squares were patterned onto PET film to show that the IPL technique can process laser-printed polymer films. The 0.25 cm by 0.25 cm black squares on the PET films were used to investigate the optimal flash power conditions and PET film thickness as shown in Figs. 2(a)-2(l). The black ink absorbed light from the flashlight and converted the light into heat so that the inks were able to thermally degrade the PET films. It is noted that the main component of laser toner ink is polyester (85 - 95%), and polyester is the same as the PET so that the thermal conductivity of toner ink and PET are similar; The thermal degradation property mainly came from the absorbed light. In these experiments, only the black part of the film burned, leaving the surrounding transparent substrate undamaged. Further, the glass transition temperature (T_g) is from 67 to 81°C and the melting temperature (T_m) of the PET films is 260°C.¹⁹ However, by increasing the thickness of the PET films to 76.2 μm and 127 μm , the PET film was no longer fully degraded in the following conditions: 127 μm in thickness using 4800 W flash power and 76.2 μm (or more) in thickness using 3400 W flash power. Conversely, the PET films were damaged when using the thinnest thickness (12.7 μm) under both flash powers. However, the films could not produce the voids at 1200 W as shown in Fig. 2(i)-2(l). This result indicated that the surface temperature increased beyond the melting point of the PET film. The heat conduction equation, below, explains why the thicker films were not able to fully degrade (also see Fig. 2(i):

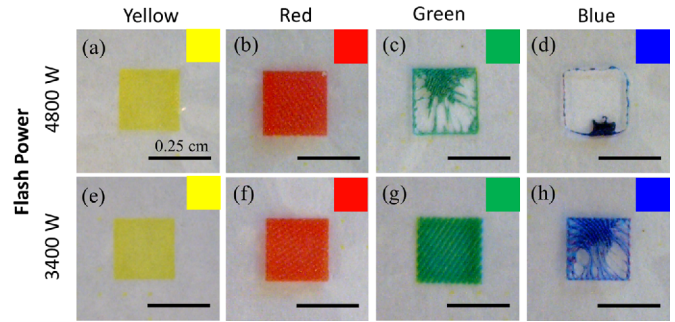


Fig. 3 Optical microscope images of the square patterns on PET films with varied colors (a) - (d) after 4800 W, and (e) - (h) after 3400 W flashlight exposure. (a), (e) yellow, (b), (f) red, (c), (g) green, (d), (h) blue. The scale bar represents 0.25 cm

$$q_z = -k \frac{\Delta T}{\Delta z} \quad (1)$$

where q_z , k , ΔT , and Δz indicate heat flux density ($\text{W}\cdot\text{m}^{-2}$), heat transfer coefficient (0.15 to 0.24 $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$), temperature difference ($T_1 - T_0$), and film thickness, respectively.²⁰ As the thickness of the PET film increases, the temperature difference increases by an order of 10 in the thickest film, which showed that this equation can qualitatively explain the phenomenon. The optimal conditions for processing the PET film were a thickness of 25.4 μm under 3400 W flash power.

Various color experiments were conducted to further investigate the effect of color, as shown in Fig. 3. Yellow, red, green, and blue colored inks, were printed in the shape of squares on PET films with a thickness of 25.4 μm and subjected to a 4800 W and 3400 W flashlight to verify the reasoning behind why black ink can create voids. The yellow and red colored inks did not burn voids in the PET film, while the green ink degraded the PET film at 4800 W and blue ink degraded the PET films at both 3400 W and 4800 W. In addition, the surface of the films after the flash of light became rougher. The most damaged film being the blue film, followed by the green and red films; the yellow one was the least damaged. This result shows that black ink can absorb a broader range of light than the other inks. Theoretically, black can absorb red, green, and blue colors; yellow absorbs blue; red absorbs green and blue; green absorbs red and blue; and blue absorbs red and green.²¹ The absorbance score equation is defined based on the area portion of absorption spectrum to explain this phenomenon, as obtained from Fig. 1(b):

$$\text{(Absorbance Score)} = \left(0.24 \times \frac{255 - I_R}{255} + 0.27 \times \frac{255 - I_G}{255} + 0.12 \times \frac{255 - I_B}{255} \right) \times 100 \quad (2)$$

where 0.24, 0.27, and 0.12 indicate the portion of intensity of the red, green, and blue colors in the absorbance spectrum, and I_R , I_G and I_B indicate the degree of red, green, and blue from 0 to 255, respectively. From Table 1, the desired absorption score can be obtained: 63 (black), 45.4 (blue), 36.3 (red), 34.6 (green), and 12.4 (yellow). These absorbance scores indicated that black could absorb the highest degree of light, followed by blue and yellow can absorb the lowest degree of light. However, as shown in Figs. 3(b), 3(c), 3(f), 3(g), the green color

Table 2 Comparison of the absorbance score in the hypothesized RGB composition from Table 1 and the resultant RGB composition from the image color extract tool

Color	Average of resultant absorbance score	Standard deviation of resultant absorbance score	Hypothesized absorbance score
Yellow	26.0	1.9	12.4
Red	35.9	1.9	39.2
Green	40.8	4.6	34.6
Blue	48.9	2.7	45.4
Black	62.6	0.5	63

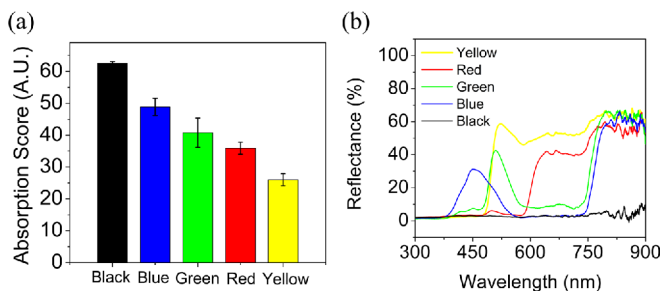


Fig. 4 (a) Absorbance score and standard deviation of black, blue, green, red, and yellow based on the resultant RGB composition from the image color extract tool, (b) UV-Vis reflectance spectrum of yellow, red, green, blue and black colors onto PET film

was damaged more than red color, which was unexpected.

To explain the unexpected result of the green and red colors, the absorbance score in the desired RGB composition from Table 1 and the resultant RGB composition from the image color extract tool are compared in Table 2 and Fig. 4(a) below. The RGB compositions of each color were obtained from random positions to calculate the average and standard deviation of the resultant absorbance score. From the calculated absorbance score and standard deviation of each resultant color, the RGB composition of both green and red were different from what was thought in Table 2. This result was due to the RGB inaccuracy of the laser printer. The absorbance scores of the resultant colors are presented in Fig. 4(a). This graph is well matched with Figs. 2 and 3 so that an absorbance score of approximately 41 is required to process PET films with 4800 W flash power and an absorbance score of about 49 is required to process PET films with 3400 W flash power. The UV-vis reflectance spectrums of yellow, red, green, blue and black colors onto PET film were measured as shown in Fig. 4(b). The yellow color reflected the light from 500 nm and the red color mainly reflected the light from 620 nm. The green and blue colors showed the maximum reflectance peak at 520 nm and 450 nm, respectively. The black color absorbed the most of light. Consequently, the yellow color could reflect the light from flashlight so that there was no void after the exposure of flashlight whereas black color could absorb the light from flashlight so that it could produce void after the exposure of flashlight. It is noted that the PET films themselves were not damaged by flashlight at all until they were covered by laser-printed inks because PET has over 90% transparency in the wavelength range of

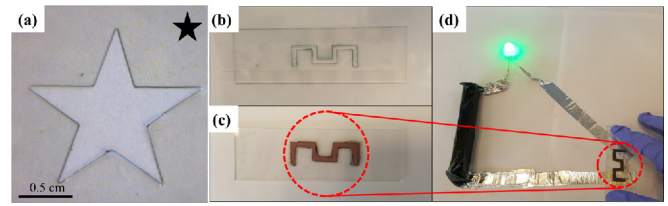


Fig. 5 (a) Star pattern created with black ink after flashlight exposure, (b) PET mask of an electrode pattern, (c) The resultant copper electrode on a glass slide created using (b) Copper nanoink, (d) LED circuit completed by the electrode from (c)

350 nm to 1000 nm.²²

A black star was printed onto PET film with a thickness of 25.4 μm and subjected to the flashlight to ensure that the masks have the capability to produce more complex patterns. As seen in Fig. 5(a), a clean, well-defined patterned void is produced, similar to the square patterns. This processing technique has a practical use as a mask for electrode patterns. This method is convenient because the masks can be made in milliseconds so when new patterns are needed, they can be made rapidly. As shown in Fig. 5(b), an electrode mask is created using the method outlined above and applied to a glass slide. Fig. 5(c) shows a copper nanoparticle ink applied to the glass slide using the PET mask. Fig. 5(d) shows the newly made electrode being used in a circuit to light up an LED light bulb. This result shows how the outlined method can be used to produce convenient, efficient, and time-effective masks. This electrode was created within 5 minutes from start to finish and was ready to use with no further preparations.

4. Conclusions

We developed an eco-friendly and rapid fabrication method for processing PET films using a xenon flashlight at room temperature under ambient air conditions. The black colored squares were patterned on PET films using a laser printer with various thicknesses of PET films and flash powers to demonstrate this technique. The heat conduction equation explained the void processing in various thicknesses of PET films. Yellow, red, green, and blue colored patterns were laser-printed on PET films with the optimal thickness to understand this phenomenon. The RGB composition of the inks and the light spectrum from the flashlight played an important role in producing heat to degrade the PET films. By defining the absorbance score and using an image color extraction tool, the amount of absorbed light was found to increase in the order yellow, red, green, blue, and black. A star pattern and an electrode-patterned mask for a copper nanoink were fabricated using the flashlight showing the practical use of the method. The masks are time-effective and especially useful when patterns are needed at a moment's notice, as the provided method can produce PET films within minutes. By using IPL, we examined the feasibility of this technique, and for future work, this approach may have many more different uses; the power provided by the flashlight could be further varied and thicker films could be used to create gradient patterns and a variety of channels of different depths with different polymer substrates.

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REFERENCES

- Kim, H.-S., Dhage, S. R., Shim, D.-E., and Hahn, H. T., "Intense Pulsed Light Sintering of Copper Nanoink for Printed Electronics," *Applied Physics A: Materials Science & Processing*, Vol. 97, No. 4, pp. 791-798, 2009.
- Yim, C., Sandwell, A., and Park, S. S., "Hybrid Copper-Silver Conductive Tracks for Enhanced Oxidation Resistance under Flash Light Sintering," *ACS Applied Materials & Interfaces*, Vol. 8, No. 34, pp. 22369-22373, 2016.
- Cote, L. J., Cruz-Silva, R., and Huang, J., "Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite," *Journal of the American Chemical Society*, Vol. 131, No. 31, pp. 11027-11032, 2009.
- Huang, J. and Kaner, R. B., "Flash Welding of Conducting Polymer Nanofibres," *Nature Materials*, Vol. 3, No. 11, pp. 783-786, 2004.
- Liao, Y., Yu, D.-G., Wang, X., Chain, W., Li, X.-G., et al., "Carbon Nanotube-Templated Polyaniline Nanofibers: Synthesis, Flash Welding and Ultrafiltration Membranes," *Nanoscale*, Vol. 5, No. 9, pp. 3856-3862, 2013.
- Kang, H., Sowade, E., and Baumann, R. R., "Direct Intense Pulsed Light Sintering of Inkjet-Printed Copper Oxide Layers within Six Milliseconds," *ACS Applied Materials & Interfaces*, Vol. 6, No. 3, pp. 1682-1687, 2014.
- Wang, L. J., El-Kady, M. F., Dubin, S., Hwang, J. Y., Shao, Y., et al., "Flash Converted Graphene for Ultra-High Power Supercapacitors," *Advanced Energy Materials*, Vol. 5, No. 18, Paper No. 1500786, 2015.
- Koga, H., Tonomura, H., Nogi, M., Suganuma, K., and Nishina, Y., "Fast, Scalable, and Eco-Friendly Fabrication of an Energy Storage Paper Electrode," *Green Chemistry*, Vol. 18, No. 4, pp. 1117-1124, 2016.
- Yoo, T.-H., Kwon, S.-J., Kim, H.-S., Hong, J.-M., Lim, J. A., et al., "Sub-Second Photo-Annealing of Solution-Processed Metal Oxide Thin-Film Transistors Via Irradiation of Intensely Pulsed White Light," *RSC Advances*, Vol. 4, No. 37, pp. 19375-19379, 2014.
- Jeon, E.-B., Park, J., and Kim, H.-S., "Ultra-Fast Annealing to Reduce the Residual Stress in Ultra-Thin Chips Using Flash Light," *Journal of Micromechanics and Microengineering*, Vol. 24, No. 4, Paper No. 045006, 2014.
- Jung, K.-W., Kawahito, Y., and Katayama, S., "Mechanical Property and Joining Characteristics of Laser Direct Joining of CFRP to Polyethylene Terephthalate," *Int. J. Precis. Eng. Manuf.-Green Tech.*, Vol. 1, No. 1, pp. 43-48, 2014.
- Chu, W.-S., Kim, C.-S., Lee, H.-T., Choi, J.-O., Park, J.-I., et al., "Hybrid Manufacturing in Micro/Nano Scale: A Review," *Int. J. Precis. Eng. Manuf.-Green Tech*, Vol. 1, No. 1, pp. 75-92, 2014.
- Bityurin, N., Luk'yanchuk, B., Hong, M., and Chong, T., "Models for Laser Ablation of Polymers," *Chemical Reviews*, Vol. 103, No. 2, pp. 519-552, 2003.
- Han, W.-S., Hong, J.-M., Kim, H.-S., and Song, Y.-W., "Multi-Pulsed White Light Sintering of Printed Cu Nanoinks," *Nanotechnology*, Vol. 22, No. 39, Paper No. 395705, 2011.
- Skorupa, W., Gebel, T., Yankov, R. A., Paul, S., Lerch, W., et al., "Advanced Thermal Processing of Ultrashallow Implanted Junctions Using Flash Lamp Annealing," *Journal of the Electrochemical Society*, Vol. 152, No. 6, pp. G436-G440, 2005.
- Reichel, D., "Temperature Measurement during Millisecond Annealing: Ripple Pyrometry for Flash Lamp Annealers," Springer, 2016.
- Park, S.-H., Chung, W.-H., and Kim, H.-S., "Temperature Changes of Copper Nanoparticle Ink during Flash Light Sintering," *Journal of Materials Processing Technology*, Vol. 214, No. 11, pp. 2730-2738, 2014.
- Bruno, T. J. and Svoronos, P. D., "CRC Handbook of Fundamental Spectroscopic Correlation Charts," CRC Press, 2005.
- Demirel, B., Yaraş, A., and Elçiçek, H., "Crystallization Behavior of PET Materials," *Balıkesir Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, Vol. 13, No. 1, pp. 26-35, 2016.
- Vlachopoulos, J. and Strutt, D., "Basic Heat Transfer and Some Applications in Polymer Processing," *Plastics Technician's Toolbox*, Vol. 2, pp. 21-33, 2002.
- Orna, M. V., "Chemistry and Artists' Colors. Part I. Light and Color," *Journal of Chemical Education*, Vol. 57, No. 4, pp. 256-258, 1980.
- Sowade, E., Kang, H., Mitra, K. Y., Wei, O. J., Weber, J., et al., "Roll-to-Roll Infrared (IR) Drying and Sintering of an Inkjet-Printed Silver Nanoparticle Ink within 1 Second," *Journal of Materials Chemistry C*, Vol. 3, No. 45, pp. 11815-11826, 2015.