Laser sintering of conductive carbon paste on plastic substrate

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Abstract. We investigate fabrication of functional conductive carbon paste onto a plastic substrate using a laser. The method allows simultaneous sintering, patterning, and functionalization of the carbon paste. Experiments are carried out to optimize the laser-processing parameters. It is shown that sheet resistance values obtained by laser sintering are close to the one specified by the manufacturer using the conventional sintering method. Additionally, a heat transfer analysis using numerical methods is conducted to understand the relationship between the temperature during sintering and the sheet resistance values of sintered carbon wires. The process developed has the potential of producing carbon-based electronic components on low-cost plastic substrates.
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Subject terms: laser sintering; carbon-based electronics; thermal analysis.

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1 Introduction

The conventional method of fabricating thick-film microelectronics involves depositing the ink or paste pattern onto a substrate via screen printing or similar means, and functionalizing it by firing the paste at high temperature in a furnace.[1] However, with the industry demand moving toward smaller feature sizes[2] and faster manufacturing times at affordable costs,[3] the conventional methods fall short in meeting these requirements. Direct-write technologies, such as MAPLE-DW (Matrix Assisted Pulsed Laser Evaporation Direct Write),[4] M^3D® (Mesoscale Maskless Material Deposition),[5] thermal spraying,[6] and Micro-Pen®,[7] were developed. All these technologies managed to successfully fabricate features with sizes ranging between 1 and 100 μm.[4] One of the drawbacks of these methods is that they require firing of the components at high temperature in order to functionalize them. This, in turn, limits the choice of substrates on which these microelectronic components can be fabricated because they could be damaged due to the high-temperature process. This is especially an important factor to consider if the application is for fabricating microelectronics on low-cost disposable plastics.

One possible solution is to sinter the components using a focused laser spot, similar to selective laser sintering (SLS).[8] SLS is a rapid prototyping process that uses a high-power laser beam to sinter powdered materials, such as metals or ceramics, in order to produce a three-dimensional part. Laser sintering can also be used for thick-film pastes. Kinzel et al.[9] demonstrated that a continuous laser can be used to sinter thick-film silver pastes to fabricate thick-film microelectronics without damaging the substrate, whose melting temperature is below the sintering temperature, whereby the choice of substrates used for this application can be expanded. They showed that the control of the temperature distribution in the inks and the substrate by varying parameters, such as laser power and the scan speed of the laser beam, lead to optimum properties of the fabricated components. Because this temperature rise is confined locally, unnecessary damage to areas outside where the functionalization is needed is avoided.

Because of the rising cost of metals today, and consequently metallic pastes, conductive carbon pastes are an attractive alternative in thick-film microelectronics[10] due to their lower cost. Another property that differentiates it from its metallic counterparts is the absence of an oxide surface. Because of the formation of an oxide layer on metallic electrodes, their performance diminishes over time.[10] Common applications of conductive carbon paste include contact pads for resistors and also as a replacement for gold contacts in mobile phones.[11] The inertness of the carbon paste also makes it attractive for biomedical devices.

In this work, we investigate processing parameters required in laser sintering to obtain the desired performance of a carbon paste wire on a plastic substrate. Although conventional sintering methods such as bulk firing would work for this case, because the substrate used has a higher melting temperature than the firing temperature of the carbon paste, the technique is applicable for substrates that have lower damage temperatures than the paste as demonstrated in Ref. 9. In addition to experimental studies, a thermal analysis is carried out using the finite element method to understand the temperature distribution required to sinter the carbon paste onto the plastic substrate.

2 Experimental Procedure

Figure 1 shows the experimental setup used in fabrication of the conductive carbon wire from carbon paste. The laser used is a 9-W continuous wave (CW) fiber laser (JDS Uniphase IFL9) with a wavelength of 1100 nm. Using a lens of 165-mm focal length, the beam spot is focused to a size of ~20 μm. The patterning process is accomplished by using

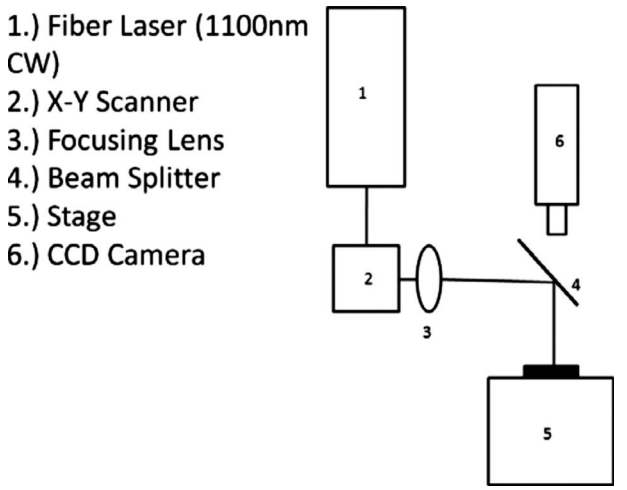

Fig. 1 Experimental setup.

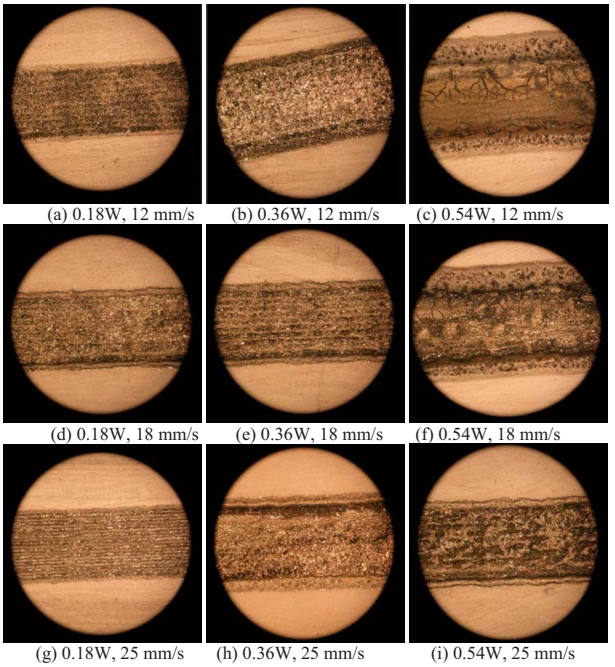

Fig. 2 Micrographs of samples at various laser powers and scanning speeds.

mirrors attached to servomotors, which along with the on-off operation of the laser, is computer controlled. The process can be observed by a CCD camera, which also assists in alignment of the sample and sintering of multiple layers, if needed.

The conductive carbon paste used for the experiments is a commercially available product, DuPont 7105. It is typically used to fabricate conductors via screen printing and seen as a cheaper alternative to metal-based inks. The composition of this ink is proprietary; however, it is deduced that because this is a conductive carbon paste, a large percentage is carbon in the form of graphite and the remaining composition would consist of organic substances used to achieve the paste form. The ink has a functionalizing temperature of 120 °C and a specified sheet resistance of 30 Ω/mm^2.[12] The substrate onto which the paste is applied is a plastic polyethylene terephthalate (PET). It has a melting temperature of 260 °C.

The paste is coated onto the substrate using a wire roller. This is a crucial step in the process because the application of the paste has to be as even as possible, which ultimately determines the consistency of sintered paste. The carbon paste–coated plastic sheets are dried in a convection oven at 90 °C for 5 min to drive off volatile organic substances in the paste.

After the drying phase is complete, the paste is then sintered by scanning the laser in the pattern that needs to be generated. In our experiments, a simple wire of length 11.08 mm and width 0.88 mm are fabricated by tracing the laser path inside the area defined by the wire dimensions. After the sintering process is complete, the portion of the paste that was not exposed to the laser beam is removed using a solvent (acetone).

After laser sintering, the paste is "functional," which can be characterized by dc resistance measurements. The lowest dc resistance that can be achieved in our study is 332 Ω. The value corresponds to a sheet resistance of 34.04 Ω/mm^2, which is close to the sheet resistance specified by the paste manufacturer using oven sintering. Detailed experimental results are discussed next.

3 Experimental Results

Varying the laser power and scanning speed would affect the fabrication process, and ultimately the dc resistance of the samples. Using a high-power/low-speed scan will result in excessive damage to the substrate due to the high temperature achieved during laser sintering. It will even result in ablation of the carbon paste. On the contrary, using a low-power/high-speed scan will result in an insufficient temperature rise for any sintering to occur. Figures 2(a)–2(i) show the different effects of the laser parameters. At all laser powers, the carbon pastes adhere to the substrate after laser irradiation, indicating certain degree of bonding between the carbon paste and the substrate. At the highest laser power shown in Fig. 2, there are visible cracks, which indicate damage to the paste and possibly the substrate. However, the micrographs alone are not sufficient to indicate the success of sintering and functionalization of the carbon paste in terms of obtaining the required conductivity. Electric conductivity or resistance measurements are needed, which are described next.

Figure 3 shows the sheet resistance measurements with respect to the scan speed for two laser powers used, 0.18 and 0.36 W. Each data point is the average of ten wires, with a standard deviation of ~10%. Two different trends can be seen. For the lower power of 0.18 W, the sheet resistance rises as the scan speed increases. This could be due to the possibility that as the scan speed increases, the exposure time of the paste to the laser beam reduces; therefore, the temperature rise that is required to functionalize the ink is never reached. Figures 2(a), 2(d), and 2(g) seem to agree with this assessment. However, for the laser power of 0.36 W, it can be seen that for a certain combination of scan speed and laser power, it is possible to obtain the minimum sheet resistance (34.04 Ω/mm^2). At slow scan

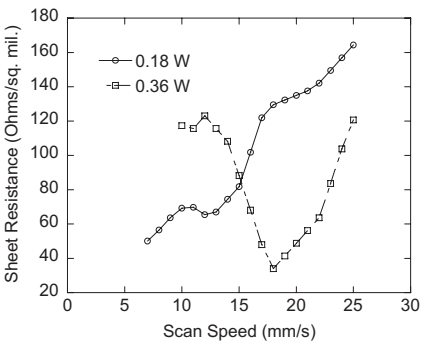

Fig. 3 Sheet resistance versus scan speed. The standard deviation at each data point is ~10%.

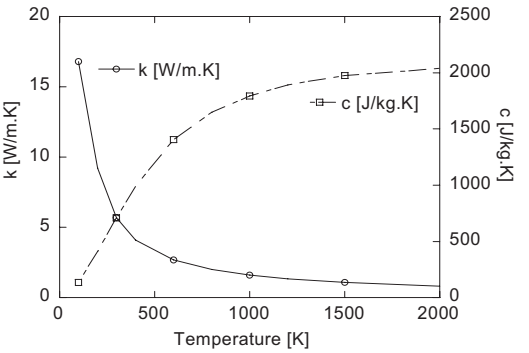

Fig. 4 Thermal conductivity and specific heat of carbon paste used in calculations.

speeds, there could be some damage to the paste and/or substrate, thus driving up the sheet resistance. As for the higher scan speeds, there is not enough exposure time to the laser energy in order for the carbon paste to be sintered or it could be possible that sintering does occur, but not enough substrate melts at the paste-substrate interface to act as a binder. It was not possible to obtain consistent resistance measurements for the laser power of 0.54 W because it caused considerable damage to the paste/substrate as seen in Fig. 2. Even if there was a trace amount of paste sintered, the wires fabricated at this energy were not continuous due to voids in the pattern. Similarly, for the laser power of 0.18 and 0.36 W, readings were not obtained below scan speeds of 7 and 10 mm/s, respectively, as severe damages occurred at these parameters.

4 Thermal Analysis

In order to better understand the physical processes occurred during laser sintering, a thermal analysis is conducted. Ideally, the carbon paste should be heated just above the functionalizing temperature and similarly the substrate near the paste/substrate interface should be heated just above its melting temperature. The rapid heating and cooling at the paste/substrate interface causes a melting and solidification of the substrate that enhances the binding of the carbon paste onto the substrate.

The thermal profile in the carbon paste and the substrate can be obtained using a numerical solution knowing the material properties. As mentioned earlier, the exact properties of the carbon paste are difficult to determine, but it can be assumed that most of it is graphite and the remaining constituents are just organic substances that evaporate during the drying phase. The thermophysical properties of graphite are used for the carbon paste[13] and the properties of PET substrate are obtained from Ref. 14. The temperature-dependant conductivity and specific heat of the carbon paste are plotted in Fig. 4. The density is considered as temperature-independent, with a value of 2210 kg/m^3. For the PET plastic substrate, the temperature-dependent property data are not available, thus, the properties at 300 K are used, with the thermal conductivity as 0.24 W/m K, the specific heat as 1000 J/kg K, density as 1370 kg/m^3, and its melting temperature as 260 °C or 533 K.

Laser heating is modeled as a volumetric heat source with a Gaussian distribution. The laser flux at any point (x,y) can be expressed by the following relationship:

$$I(x,y,t) = \frac{2P}{\pi r_0^2} \exp\left[-2\frac{(x-x_0-v_x t)^2+(y-y_0)^2}{r_0^2}\right], \quad (1)$$

where P is the laser power, r_0 is the beam radius $(1/e^2)$, v_x is the scan speed along the x-direction, x_0 and y_0 are the original location of the center of the laser spot, and t is the time. Using Lambert's law of absorbance which accounts for the amount of attenuation due to the reflectivity of the surface, the laser heat flux inside the paste is expressed as

$$q(x,y,z,t) = (1-R_f)I(x,y,t)\exp(-\alpha z), \quad (2)$$

where R_f is the surface reflectivity of the paste and α is the absorption coefficient. The absorption coefficient value used for the simulation is 3.2×10^6 cm^{-1}.[15] A surface reflectivity of 0.1 is used since the coated surface is black. The volumetric heat source term due to the absorbed laser energy is obtained by differentiation of the laser heat flux with respect to the absorption depth, z,

$$Q_{\text{abs}} = -\frac{dq}{dz} = \alpha(1-R_f)I(x,y,t)\exp(-\alpha z). \quad (3)$$

The governing heat conduction equation can then be expressed with the consideration of the laser absorption term

$$\rho c_p \frac{\partial T}{\partial t} = \nabla(k\,\nabla\,T) + Q_{\text{abs}}, \quad (4)$$

where c_p is the specific heat, ρ is the density and k is the thermal conductivity of the material.

The solver used for simulation is ANSYS (ANSYS Inc., Canonsburg, PA). The simulation domain is 150 μm long in the x direction, the paste thickness is 3 μm, and the substrate is represented by a 25-μm thick layer. The $z=0$ μm position locates at the paste-substrate interface. The laser beam, which is incident normally on the paste, is traced starting from 50 μm from the edge (at $x=0$) for 100 μm.

Figures 5(a)–5(c) show the comparison of three transient thermal profiles for a scan of the same power but different

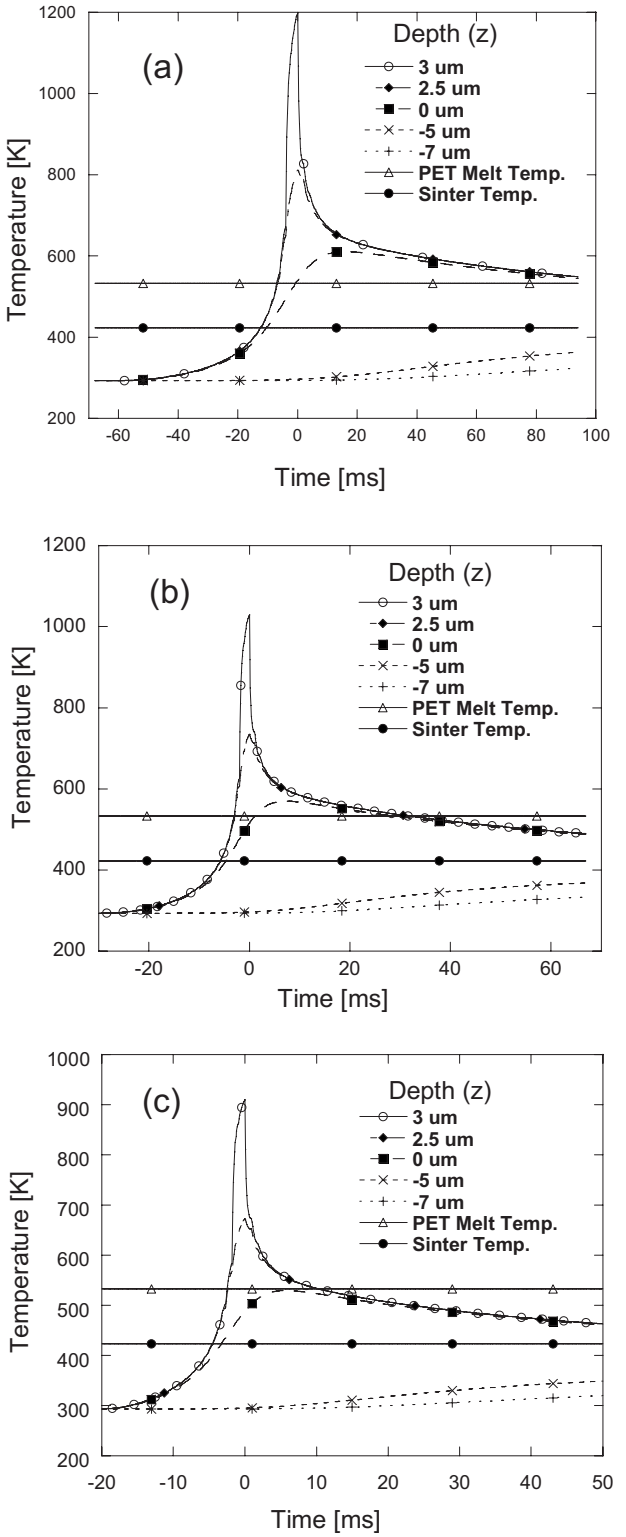

Fig. 5 Transient thermal profile of conditions of (a) 0.36 W, 12 mm/s, (b) 0.36 W, 18 mm/s, and (c) 0.36 W, 25 mm/s.

velocities. The value when time equals to zero ($t=0$ ms) corresponds to when the laser is directly above the point of consideration.

The computed transient thermal profiles can be used to explain the correlation between the processing parameters and the performance of the fabricated component. It should be noted, however, that because the exact thermophysical properties of the conductive carbon paste are not known, the calculated thermal profiles are not meant to represent the process exactly, but instead assist in explaining the experimental results. Having said that, the thermal simulation results seem to be in good agreement with the experimental results. As noted in the experimental results, the lowest sheet resistance was obtained when the laser power was 0.36 W scanning at a speed of 18 mm/s. Figure 5(b) shows the corresponding transient thermal profile for that condition. It can be seen that the temperature at the interface ($z=0$ μm), the temperature rises above the PET melting point for a time in the order of a few milliseconds. The melting and resolidification in that short duration of time causes the plastic to act as a binder, allowing the carbon paste to adhere to the substrate. Similarly, the experimental results can be explained for the cases where the scan speed is too low or too high. From Fig. 5(a), which shows the case of low scan speed, it can be seen that the interface temperature rises above the melting temperature of the substrate and the time taken to cool down to a temperature below the melting temperature is longer. This can be the reason for the pattern obtained in Fig. 2(b), where bubblelike patterns are seen. As for the high scan speed case of 0.36 W, 25 mm/s, the exposure time is too short for there to be a necessary rise in temperature at the interface. The temperature barely reaches the melting point of the substrate but never surpasses it. This causes insufficient binding of the carbon paste onto the substrate, which can be an explanation for the rise in sheet resistance values at higher scan speeds.

Another observation is that only a small region below the interface ($z<0$ μm) is affected by laser heating. The temperature rise in PET is confined within a few micrometers from the interface. In a sense, it is advantageous when only the surface of the substrate has its temperature raised above its melting point, in order to create the binding effect necessary for the carbon paste to remain on the substrate. The rest of the substrate is saved from unnecessary damage.

Figures 6(a) and 6(b) provide a better illustration of the penetration of thermal energy with respect to depth. The maximum temperatures obtained versus depth are shown for different laser power and scan speed. The vertical black line intersecting at 0 μm represents the interface between the paste and the substrate. For all the cases, the temperature in the paste is above the required sintering temperature. However, what differentiates the measured resistances from one another is how well the carbon paste has bound to the substrate. For example, when using a laser power of 0.54 W and 12 mm/s, even though the paste has been exposed to temperatures above the required sintering temperature, the substrate layer as deep as 2 μm is raised above the melting temperature. This phase change appears to be damaging to the substrate and contributes to uneven patterning of the sintered paste.

Similarly, for very low laser power and high scan speed, the sheet resistance values are also high because it is possible that the paste-substrate interface will never reach the melting temperature of the substrate and therefore paste does not bound well. These calculations show that with the understanding of the temperature profiles in the paste and

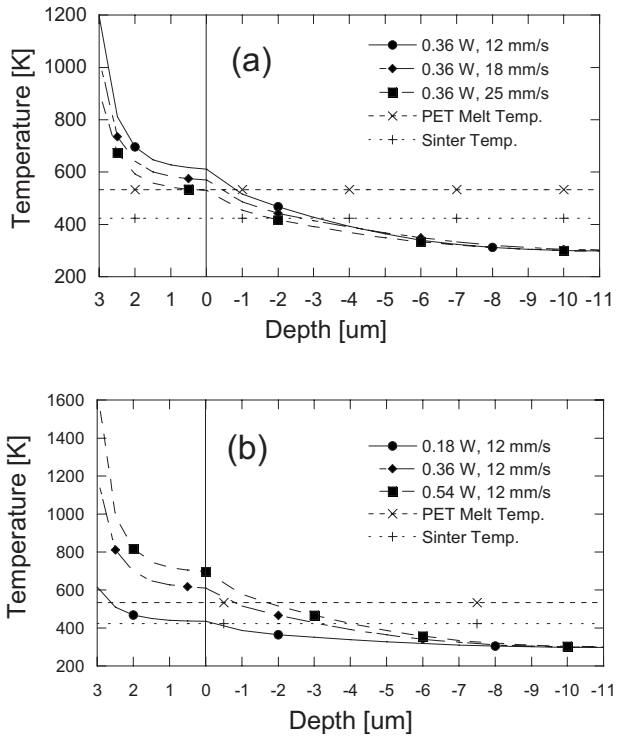

Fig. 6 (a) Maximum temperature obtained at different scan speeds and (b) maximum temperature obtained at different laser powers.

the substrate, it is possible to optimize laser parameters in order to obtain the best resistance values in sintered carbon wires.

5 Conclusion

This work investigated processing parameters required in sintering conductive carbon paste onto a plastic substrate. The dc resistance achieved using laser sintering is similar to what can be obtained from bulk firing; however, the laser sintering technique provides the advantage of combing sintering and pattering steps in one. A greater understanding of the effects of the processing parameters is obtained by performing a finite element analysis of the transient thermal process involved. The ideal process would be heating the paste-substrate interface above the melting point of substrate for a short period of time, on the order of milliseconds, in order to enhance the binding of the carbon paste onto the substrate, which can be achieved by proper combinations of the laser power and scan speed.

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