A THERMAL INVESTIGATION ON CONDUCTIVE SILVER INK TRACKS CURED ON FLEXIBLE SUBSTRATES BY REPEATING IRRADIATIONS OF ND:YAG LASER AT THE WAVELENGTH OF 532 NM

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Abstract

The development of the plastic electronics industry has drawn great interest and inspired technology innovations in a broad area. This has stimulated the rapid development of flexible circuitry manufacturing technologies, including advances in conductive inks, printing technology and most importantly the novel curing technology - laser based curing (or Laser Direct Write). This has the ability to replace the conventional environmentally damaging and time consuming chemical etching method in current Printed Circuit Board (PCB) manufacturing.

This work presented in this paper is an investigation into the Nd:YAG laser curing process at the wavelength of 532 nm of particulate silver inks. A mathematical approximation of key physical properties has been developed based on the presented experimental research for use in a finite element model (FEM) simulation. 532 nm has shown benefits in protecting the flexible substrate used from thermal damage, owing to the high transparency of the wavelength through the substrate material. In this paper, liquid-phase particulate silver ink tracks deposited on flexible substrates were irradiated by laser along the track geometry. Repetition of the laser beam scanning was found to produce a smooth and fully cured sample and further reduced the track’s electrical resistivity.

Introduction

Printed Circuit Boards (PCBs) are a key component in almost every electronic and electrical device. The electronic components are connected via electrical conductive tracks on a baseboard which is made from an insulating material. Assemblies in which the application could be used range from personal entertainment, telecommunications and IT terminals to military defence equipment. Fabricating a PCB requires a series of processing steps including CAD design, panel preparation, image transfer, etching, board drilling, coating and testing before a final finished board is manufactured [1]. Each processing step generates waste which is harmful to both personal health and the environment. The subtractive method which dominates in conventional PCB manufacturing produces more metal waste than additive methods [2]. Thus a new significantly more environmentally friendly technology – Laser Direct Write (DW) is being investigated as a suitable replacement to conventional methods. In terms of PCB manufacturing, Laser DW refers to the rapid process that cures a liquid ink track and makes it electrically conductive on top of an insulating substrate. Laser irradiation results in ink track solidification when the solvent is removed from the ink, and the resin is cured by cross-linking. The track then becomes electrically conductive due to an increased particulate silver contact as the volume of the track is thus reduced [3].

Multiple pass laser beam scanning has been shown to produce a smooth and fully cured sample with lower resistivity when compared with single pass laser curing. Multiple pass scanning strategies also give an improved curing result in terms of denser silver particle combinations and prevent damage to the substrate caused by extensive heat generated as observed in a single pass curing strategy.

Laser direct write can also be used in the production of flexible electronic circuitry such as that used in flexible displays. Using a laser wavelength at 532 nm can prevent thermal damage to the flexible substrate owing to the high transparency at 532 nm [4,5]. A typical polymer substrate – Polytetrafluoroethylene (PET), for example, enables PCB manufacturing development towards to a new market place with advantages in weight and flexibility.

Objectives
The objective of this investigation is to develop mathematical approximations based on experimental results for key process parameters that reflect the dynamic changes of material physical properties during multiple scanning by laser radiations. During the process of multiple pass laser curing of particulate silver inks, physical properties for the material being processed such as thermal conductivity, electrical resistivity, specific heat capacity, density, mass, etc. are subject to change with increasing processing time. Therefore having these key dynamic physical properties such as thermal conductivity and specific heat capacity mathematically defined will increase the accuracy of the finite element model (FEM).

Assumptions Required For Generation of the FE Model

The silver ink can be described as a mixture composition with approximate weight percentages of 60%, 26%, 14%, for silver flakes, epoxy resin system, and solvent, respectively. The polymer substrate – Polyethylene terephthalate (PET) was chosen as the substrate due to its weight and flexibility.

1. Thermal Conductivity

The mechanism of laser curing will result in the value of thermal conductivity of the silver ink track changing while the laser beam is scanning along the ink track geometry. This occurs due to a change from liquid to solid and an associated change in composition of the ink. Thermal conductivity is extremely low at the beginning of the laser scan, but once the dominant heat transfer mechanism changes from convection to conduction at time \( t_c \), the thermal conductivity increases with increasing number of laser scanning passes, and eventually becomes highly thermally conductive by the end of laser cure [6].

\[
\sigma = \frac{1}{\rho} = \frac{\ell}{R \cdot A} \quad (1)
\]

\[
\frac{\kappa_{\text{ink}}}{\sigma_{\text{ink}}} = \frac{\kappa_{\text{bulkAg}}}{\sigma_{\text{bulkAg}}} = L \cdot T \quad (2)
\]

\[
\frac{\kappa_{\text{ink}}}{\sigma_{\text{bulkAg}}} = \frac{\ell}{\rho_{\text{bulkAg}}} \cdot \frac{L}{R \cdot A} \quad (3)
\]

Where:
- \( \ell \) = length of the piece of material,
- \( \sigma \) = electrical conductivity of the material,
- \( \rho \) = electrical resistivity of the material,
- \( \kappa \) = thermal conductivity of the material,
- \( \Delta T \) = temperature change of the ink due to heat absorption.

According to Wiedemann-Franz law, the ratio of thermal conductivity of silver ink track and bulk silver is proportional to the ratio of electrical conductivity, thus the dynamic changes of the thermal conductivity during the laser scanning process can be linked to the electrical conductivity changes of the silver ink track.

2. Specific Heat Capacity \( c_{\text{ink}} \) For Silver Ink Track

Another important parameter that needs to be defined is the ink’s specific heat capacity \( c_{\text{ink}} \). Like the ink’s thermal conductivity, the specific heat capacity also changes dynamically during laser cure as the composition changes.

\[
C_{\text{ink}} = \frac{Q}{\Delta T} = \frac{Q/\Delta t}{\Delta T/\Delta t} = \frac{Q}{\Delta t} \cdot \frac{\Delta t}{\Delta T} = \frac{\alpha \cdot P_{\text{laser}} \cdot \Delta t}{\Delta T} = \frac{\alpha \cdot P_{\text{laser}}}{R} \quad (4)
\]

\[
c_{\text{ink}} = \frac{C_{\text{ink}}}{m_{\text{ink}}} = \frac{C_{\text{ink}}}{V_{\text{ink}} \cdot \rho_{\text{ink}}} \quad (5)
\]

Where:
- \( C_{\text{ink}} \) = heat capacity of silver ink track,
- \( C_{\text{ink}} \) = specific heat capacity of silver ink track,
- \( \alpha \) = absorption coefficient,
- \( P_{\text{laser}} \) = the laser output power,
- \( V_{\text{ink}} \) = ink track’s volume,
- \( \rho_{\text{ink}} \) = ink’s density,
m_{ink} = \text{mass of the ink track},

\Delta t = \text{the total scanning time per each pass.}

The heat capacity could be calculated by given values of temperature changes of each scanning pass \(\Delta T/\Delta t\). The specific heat capacity is taken as the ratio of absorbed laser energy over scanning time per pass and the temperature difference over the scanning time per pass.

3. Thermal Absorption Coefficient \( \alpha \)

Silver ink absorbs the thermal energy from the incident laser beam. As Shuo suggested [7], the absorption coefficient is a function of the inks composition during the laser scan.

\[
\alpha = \begin{cases} 
(1 - Ag\%)\alpha_s + (1 - \alpha_r)\alpha_r & \text{(before solvent removal)} \\
(1 - Ag\%)\alpha_r & \text{(after solvent removal)} 
\end{cases}
\]  

\( \alpha_s \) and \( \alpha_r \) refer to the absorption coefficient to solvent and epoxy resin of the ink, respectively, and can be calculated using Beer-Lambert law [6,7]. Ag\% refers to the volume percentage of silver flakes within the ink. During the laser scanning process, the composition of the ink will change, and the change in ink’s composition will further affect the thermal absorption coefficient and volume.

**Experimental Procedure For Determining Physical Properties Of The Ink Used**

The liquid silver ink was dispensed onto the PET substrate by using a screen-printing method (figure 1) [6,7]. A metal panel was used as stencil and placed on top of the PET and held by tape leaving a negative track-shape image. The silver ink was drawn above this negative image using a scraper. On removal of the stencil a finished silver ink track sample was produced with dimensions 120mm long and 3.5mm wide.

As previously described by the Wiedemann-Franz law, the thermal conductivity of silver ink during the laser scan could be calculated by the relationship to electrical resistance. The thermal conductivity of bulk silver is 429 W mK\(^{-1}\) [7], and the electrical resistivity for bulk silver is 15.87e-9 \(\Omega\) m [8], the cross sectional area of the ink track was calculated as the thickness of ink track multiplied by the width of the track. The ink track electrical resistance was measured using a multimeter connected to the two ends immediately after each scanning pass (figure 4). In order to investigate how the laser affects the thermal conductivity, three different laser output powers were selected (13.98W, 17.94W, and 24.10W). All the samples were cured using the same scanning speed (15mm/sec).
Figure 4. Resistance of ink track measurement, this was measured immediately after the laser scan of each pass.

Table 1. Process parameters investigated.

<table>
<thead>
<tr>
<th>Laser Output Power (W)</th>
<th>Scanning speed (mm/s)</th>
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<tbody>
<tr>
<td>13.98</td>
<td>15</td>
</tr>
<tr>
<td>17.94</td>
<td>15</td>
</tr>
<tr>
<td>24.10</td>
<td>15</td>
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According to equations (4), (5) and (6) above, if the temperature difference over each scanning pass $\Delta T/\Delta t$ is known, the specific heat capacity of the ink could be calculated. The temperature differences were measured by placing a K-Type thermocouple within the ink track, then the reading of temperature differences were monitored and recorded every 3 ms in an Agilent data logger (figure 5).

Figure 5. Illustration of temperature difference $\Delta T/\Delta t$ measurement, the type K thermocouple was placed within the ink for the purpose of monitoring the temperature change of the ink.

Results And Discussion

The curing result for a silver ink track is dependent on the selection of laser output power and scanning speed. From experimental study, a higher laser output power and slower scanning speeding will more effectively cure an ink, resulting in greater electrical conductivity. However, this curing strategy increases the chance of bubbling on the top surface of the ink track due to extensive heat flux along the scanning geometry rapidly liberating the evaporated solvent. This bubbling of the top surface is detrimental to high-frequency applications.

Figure 6. Change in thermal conductivity of ink based on experimental data.

The silver ink track becomes thermally conductive only after a critical time $t_c$ has been reached. This time $t_c$ is reciprocal to laser output power in that the larger the output power, the shorter the time the ink track takes to become thermally conductive.

Figure 6 shows how thermal conductivity changed with increasing scanning pass number for a constant scanning speed. The shape of the thermal conductivity curve can be estimated by using a root function for a mathematical approximation of the form:

$$
K_{ink} = \begin{cases} 
0 & (t < t_c) \\
\frac{t}{P_{laser}} & (t \geq t_c)
\end{cases}
$$

(7)

$$
t_c \propto \frac{1}{P_{laser}}
$$

(8)

Where:

$\alpha, \beta = \text{coefficients},$
\[ P_{\text{laser}} = \text{laser output power}, \]
\[ t = \text{effective laser scanning time}, \]
\[ t_c \] is defined as the critical time at which thermal conductivity takes over from convective heat transfer i.e. when the ink has lost sufficient solvent.

Figure 7 shows the temperature difference $\Delta T/\Delta t$ monitored by thermocouple over a single scanning pass, the shape of the function could be seen as inverse-chi-squared distribution for mathematical approximation.

\[
T(t; \nu) = \frac{2^{-\nu/2} e^{-t^2/(2\nu)} (1/t)^{1+\nu/2}}{\Gamma(\nu/2)}
\]  

(9)

\[ \nu \] is also a variable and is inversely proportional to scanning pass number and laser output power.

**Use Of Derived Parameters in the FE Model**

The parameters derived from the preceding experiments were used to generate a FE model with COMSOL 4.0. This provides a powerful tool that enables precise and smooth simulation, as well as integrating various applications such as MATLAB programming software.

This model was used to generate graphs for comparison with experiment. In the COMSOL modelling environment, the material physical properties could be manually defined for optimising the simulation results. For the ease of simulation the following assumption is made; the laser curing process is defined as a 3 pass laser scanning process in which the first pass removes the organic solvent of the ink, the second pass of scan cross links the epoxy resin, and the third pass increases the degree of inter-particle connections.

Figure 8. Change in temperature over each scanning pass for the first 3 passes, it simulates the multiple pass laser curing process with the output power of 17.94W and the laser beam traverse speed at 10mm/s.

Figure 8 shows the simulated temperature rise in the ink track. The derived dynamic key physical properties used in the model are also given in figures 9 - 11.

It can be seen in figure 8 that the rate of temperature change is lower in first few passes, as solvent is still being evaporated from the ink, which increases the track’s thermal conductivity. With increased number of scanning passes, or increased laser output power, the rise and fall times reduce, and the temperature at peak becomes higher, this is consistent with the simulated higher thermal conductivity with time, as shown in figure 9. As a result of the increased thermal conductivity, the time above minimum cross linking temperature and the corresponding maximum temperature becomes higher and helps to cross link the epoxy resin. At high scanning pass numbers, the larger proportion of silver in the ink compared to the uncured state has the effect of reducing the heat capacity of the ink track and also reducing the absorption coefficient, how this is simulated can be seen in figure 10. In addition by combining equations (4), (5) and (6), the change in specific heat capacity of the ink can also be estimated and included in the simulation (Figure 11).
Conclusions
An experimental-based investigation has been conducted for the purpose of deriving novel mathematical equations for dynamic physical properties of particulate silver inks during laser curing for FEM simulation.

The silver ink, composed of silver flakes, epoxy resin, and solvent, was dispensed onto a flexible PET substrate and cured using a DPSS Nd:YAG laser at the wavelength at 532 nm.

Based on the experimental result, a relationship was derived for the ink tracks key dynamic physical properties thermal conductivity, absorption coefficient and specific heat capacity. Initial results from the model show a good agreement with observed phenomena.

The derived mathematical equations for dynamic physical properties defined in this paper have built a foundation for further FEM simulations. This will benefit the ongoing research by providing an insight into the curing mechanism, more (virtual) experimental freedom and a finer degree of control.

References


Meet the Author

Liwei Fu is currently carrying out his Ph.D research at the laser group, the University of Liverpool, UK in investigating potential laser curing mechanisms based on FEM simulation and experimental research. Liwei received his Master degree in Telecommunications from Swansea University, UK.