Electronic Supplementary Information

Flexible thermistors: pulsed laser induced liquid phase sintering of spinel Mn-Co-Ni oxide films on polyethylene terephthalate sheets

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Temperature variations during laser irradiation can be described by the heat diffusion equation simplified to describe one-dimensional heat flow:

\[ \rho C \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2} + aI(z,t) \]

where \( T \) is the temperature function at time \( t \) and depth \( z \), \( \rho \) is the mass density, \( C \) is the specific heat capacity, \( \alpha \) is the optical absorption coefficient, \( \kappa \) is the thermal conductivity, and \( I(z,t) \) is the laser power density. The laser power \( I(z,t) \) is given by:

\[ I(z,t) = I_0(t) \cdot (1 - r) \cdot \exp(-\alpha z) \]

where \( r \) is the reflectance. The contribution from the incremental absorbance of the films caused by reflectance at the substrate surface was also included in the laser power distribution. \( I_0(t) \) is described as a smooth pulse approximated by:

\[ I_0(t) = I_0 \cdot \left( \frac{t}{\tau} \right)^\beta \cdot \exp \left( \beta \left( 1 - \frac{t}{\tau} \right) \right) \]

where \( I_0 \) is the incident pulse power density, \( \tau \) is the pulse duration (KrF: 26 ns), and \( \beta \) determines the temporal pulse shape (KrF: 6.0). We carried out numerical simulations for the temperature variation for the excimer laser irradiation process using a difference approximation based on the above equations. The initial conditions were \( T = 25 \, ^\circ\text{C} \) at \( t = 0 \, \text{s} \) and \( T = 25 \, ^\circ\text{C} \) at the bottom of the substrate.

The boundary condition was \( \kappa \frac{\partial T}{\partial z} = 0 \) at the interfaces. The physical constants used in the calculations are listed in Table S1.

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Fig. S1: The thermal conductivity, mass density and heat capacity of air. The red lines represent the fitting curves.
Table S1 Physical properties used in numerical simulations.²⁻⁴

<table>
<thead>
<tr>
<th>Material</th>
<th>α (cm⁻¹)</th>
<th>r (W cm⁻² K⁻¹)</th>
<th>ρ (g cm⁻³)</th>
<th>C (Jg⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₃O₄</td>
<td>9.58×10⁴</td>
<td>0.191</td>
<td>0.057</td>
<td>4.856</td>
</tr>
<tr>
<td>Air</td>
<td>3.34×10⁻⁶</td>
<td>0.00186</td>
<td>1.57–10⁻⁴</td>
<td>0.18–1.98×10⁻³</td>
</tr>
</tbody>
</table>

The thermal conductivity, mass density and heat capacity of air were obtained by the fitting of data from -100 – 1600 °C (Fig. S1).

Figure S2 shows the FESEM image for the MCN film that was irradiated by KrF laser at 55 mJ·cm⁻² for 50 pulses. The small nano-particles on the surface and nano-pores were clearly confirmed. Conversely, such kind of nanostructures was not observed in the MCN film prepared by the MCN dispersion without the MCN-solution (Fig. S3).

Fig. S2: The enlarged view of FESEM image for the MCN film irradiated at 55 mJ·cm⁻² for 50 pulses.

Fig. S3: The FESEM image for the MCN film coated by using the starting MCN dispersion without the MCN-solution, which irradiated at 55 mJ·cm⁻² for 600 pulses.
Figure S6: Temperature variation of the electrical resistance, $R$ (MΩ), for the three MCN films on PET substrates prepared at 55 mJ·cm$^{-2}$ for 600 pulses. The solid lines are Arrhenius equation fitting curves.

Figure S4 shows the electrical resistance of MCN-T and MCN-L films before/after the resin coating. The coated resin filled the nano-pores, and they would contribute the resistance reduction. The electrical resistivity of MCN layer with the pores was calculated by using a simple serial-parallel circuit model as shown in Fig. S5a. We assumed the MCN layer with the cuboid size of 20 µm × 20 µm × 100 nm, which consisted of 100 nm cube resistive elements. The resistance of each element for MCN, resin (methylcellulose) and pore (air) were $10^{-5}$ Ω, $10^5$ Ω and $10^{11}$ Ω, respectively. The pores were produced randomly in the matrix for 0.5–2.5% (Fig. S5b). The calculation showed the difference of resistivity between the models with/without the resin coat. When the pore density ($p$) was sufficiently small ($p \leq 0.5\%$), the difference was ignorable. However, it much increased with the increasing $p$ (= increasing pore number and size). This would reflect the experimental result as shown in Fig. 4a. Too large $p$ ($p \geq 2.5\%$) caused complete disconnection of conduction pathways (MCN) and the resistivity was calculated to be huge (= insulator).

References
2 EngineeringToolBox: http://www.engineeringtoolbox.com/air-properties-d_156.html.
5 Materials Safety Data Sheet Solution Center: http://www.msds.com/.