A new method to directly print out a solidified electronic circuit through low-melting-point metal ink is proposed. A functional pen with heating capability was fabricated. Several typical thermal properties of the alloy ink Bi$_{75}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ were measured and evaluated. Owing to the specifically selected melting point of the ink, which is slightly higher than room temperature, various electronic devices, graphics or circuits can be manufactured in a short period of time and then rapidly solidified by cooling in the surrounding air. The liquid–solid phase change mechanism of the written lines was experimentally characterized using a scanning electron microscope. In order to determine the matching substrate, wettability between the metal ink Bi$_{75}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ and several materials, including mica plate and silicone rubber, was investigated. The resistance–temperature curve of a printed resistor indicated its potential as a temperature control switch. Furthermore, the measured reflection coefficient of a printed double-diamond antenna accords well with the simulated result. With unique merits such as no pollution, no requirement for encapsulation and easy recycling, the present printing approach is an important supplement to current printed electronics and has enormous practical value in the future.
1. Introduction

Printed electronics is of growing scientific interest for applications in a number of areas, including transistors [1,2], antennae [3], printed circuit boards (PCBs) [4], light-emitting diodes [5–7], radio frequency identification [8], photovoltaics [9], sensors [10,11], memories [12] and so on. Among the various printing techniques, such as micro-contact printing [13], nanoimprinting [14], screen printing [15], stencil printing [16,17], drop-on-demand inkjet printing [18] and roll-to-roll printing [19], direct additive printing has many advantages such as low cost and easy operation compared with the conventional vacuum deposition and photolithographic patterning methods [20]. In recent years, Russo et al. [21] demonstrated a facile pen-on-paper method to directly create flexible printed electronics using conductive silver ink. Although conductive tracks can be directly written upon paper via this method, there still exist several limitations that need to be overcome. The preparation of conductive silver ink is a complicated process and the ink needs to be stored in properly sealed containers. To achieve better properties of the printed silver ink, a certain annealing temperature and time are necessary. For example, only after annealing to higher temperatures (greater than or equal to 170°C) can one expect a comparatively ideal electrical resistivity (4.34 × 10⁻⁸Ω m) of the silver ink (50 wt% silver). Undoubtedly, write and play cannot be realized easily via this type of conductive silver ink. Also, recycling the printed silver ink is another difficult task that produces material waste when printing with this ink. Dickey et al. [22] investigated a type of liquid metal GaIn₂₄.₅ (melting point approx. 15.₇°C), which is in the liquid state at room temperature, and evaluated its rheological behaviour and oxidation properties. Zheng et al. [23] and Boley et al. [24] used such an ink in direct writing technology. However, the patterns printed with this ink need to be packaged or they can be easily damaged when exposed to air because of the flowability of the ink. Similar to the conductive silver ink, GaIn₂₄.₅ ink is not easily recycled after printing. In order to provide a new candidate ink for pen-on-paper writing technology, a type of alternative Bi-based alloy, Bi₃₅In₄₈.₆Sn₁₆Zn₀.₄ [25], is introduced as the printing ink in this article. The measured melting point of Bi₃₅In₄₈.₆Sn₁₆Zn₀.₄ is 58.₃°C, which is slightly lower than the Bi–In–Sn alloys (approx. 60°C) [26]. Bi₃₅In₄₈.₆Sn₁₆Zn₀.₄ is a non-toxic material, and the four constituent metals (Bi, In, Sn and Zn) are in widespread use [27–30], e.g. Bi compounds are widely used in cosmetics and pharmaceuticals [31]. This metal ink has unique merits such as it is easy to prepare, it has high electrical conductivity, it is non-polluting and it is easy to recycle. Direct writing with such an ink will have important practical significance and application value to supplement the current PCB manufacturing technology.

2. Material and methods

(a) Preparation of Bi₃₅In₄₈.₆Sn₁₆Zn₀.₄ metal ink

The four metals (bismuth, indium, tin and zinc) with purity above 99.₉₉% (4N) were purchased from Shenzhen Zhongjin Lingnan Non-ferrous Metal Co., Ltd, China, and Wuxi Bokai Analytical Instrument Manufacture Co., Ltd, China, for making the alloy ink. They were weighed according to the ratio of 35:48.₆:16:0.₄. Then, these pure metals were put in a beaker for 5 h at 245°C in an electric vacuum drying oven. The mixture was stirred in the beaker, which was then put in a water bath at 85–90°C for 30 min. Finally, the beaker was placed in the electric vacuum drying oven for 2 h to further ensure a well-mixed alloy solution. This preparation process, which took only half of a day, is much simpler than the preparation of silver nanoparticles [32], especially when mass production is required.

(b) The structure of the heating pen and thermal properties of the metal ink

The heating pen loaded with Bi₃₅In₄₈.₆Sn₁₆Zn₀.₄ needs to be heated since the melting point of Bi₃₅In₄₈.₆Sn₁₆Zn₀.₄ (approx. 58.₃°C) is slightly higher than room temperature. The external appearance of the heating pen is shown in figure 1a. The pen container loaded with liquid metal
ink is installed in the aluminium heating muff. A plug is located at the tail of the pen holder to stopper the pen container. The aluminium heating muff is wound with a constantan wire which is powered by a DC (direct current) regulated power supply. The sectional structure of the heating pen is shown in figure 1b. The pen holder is wrapped with a yellow high-temperature adhesive tape to reduce heat dissipation and to fix the constantan heating wire. Joule energy is generated when current is passed through the constantan wire and the aluminium heating muff and the liquid metal ink will thus be heated. The temperature of the heating pen is monitored via a k-thermocouple which is located in the middle of the pen holder. The k-thermocouple is connected to a data acquisition instrument from which the temperature change of the pen holder can be observed.

Figure 2a illustrates the change in dynamic viscosity of the liquid metal ink Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ at different temperatures. The measurements were performed with a high-temperature molten metal viscometer fabricated at Shandong University based on an oscillating-cup method [34]. The dynamic viscosity of the ink is measured at five temperature points (74°C, 95°C, 150°C, 203°C and 295°C) and measurement at each temperature point is repeated three times. It can be seen that the dynamic viscosity of the ink decreases with increasing temperature, and the descent velocity

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**Figure 1.** (a) The external appearance of the heating pen loaded with Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ liquid metal ink. Inset: The macrograph of the pen nib. Scale bar is 5 mm in length. (b) The sectional structure of the heating pen. (Online version in colour.)

**Figure 2.** (a) The dynamic viscosity ($\gamma$) of the liquid metal ink Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ measured as a function of temperature ($T$). (b) The electrical conductivity ($\kappa$)–temperature ($T$) and the thermal expansion rate ($\Lambda$)–temperature ($T$) measurement curves of the liquid metal ink Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ in the solid state. The data are from [33]. (Online version in colour.)
changes from fast to slow. When the temperature of the heating pen becomes too low, the metal ink cannot smoothly flow when writing because of its high viscosity. On the other hand, when the temperature of the heating pen is too high, the metal ink will flow uncontrollably even when not writing because of its low viscosity. In our experience, the temperature of the heating pen should be regulated within the range of approximately 70–80 °C (the corresponding dynamic viscosity range is from approx. 4.1 to 3.9 mPa s) to write/print smoothly.

The electrical conductivity (κ) and the thermal expansion rate (Λ) of Bi<sub>35</sub>In<sub>48.6</sub>Sn<sub>16</sub>Zn<sub>0.4</sub> in the solid state are measured by a four-probe electrometer method using a physical property measurement system (PPMS, Quantum Design) at a heating rate of 5 °C min<sup>−1</sup>. It can be observed that, with the increase of T, κ approximates to a linear decrease while Λ approximates to a linear increase. The electrical conductivity of Bi<sub>35</sub>In<sub>48.6</sub>Sn<sub>16</sub>Zn<sub>0.4</sub> is 7.31 × 10<sup>6</sup> S m<sup>−1</sup> at room temperature. This is approximately twice that of GaIn<sub>24.5</sub> (3.36 × 10<sup>6</sup> S m<sup>−1</sup>) [35], which was used as the printing ink by Zheng <i>et al.</i> [23], and approximately 14 times that of conductive silver ink (50 wt% silver, 5.03 × 10<sup>5</sup> S m<sup>−1</sup>), which was used by Russo <i>et al.</i> [21] before heat treatment. The comparatively higher electrical conductivity of Bi<sub>35</sub>In<sub>48.6</sub>Sn<sub>16</sub>Zn<sub>0.4</sub> makes it suitable for writing circuit lines. It can be seen from the Λ–T measurement curve that Bi<sub>35</sub>In<sub>48.6</sub>Sn<sub>16</sub>Zn<sub>0.4</sub> expands when heated and contracts when it is cold. The measurement curve shows excellent linearity, and the thermal expansion coefficient is approximately 30.5 × 10<sup>−6</sup> per °C at room temperature.

3. Experimental results

(a) Wettability between liquid metal ink and several substrates

To determine the appropriate substrates on which to perform direct-write technology with the heating pen, wettability between Bi<sub>35</sub>In<sub>48.6</sub>Sn<sub>16</sub>Zn<sub>0.4</sub> and different substrates was investigated. The measured RMS (root mean square) roughness of the five substrates—mica plate, PVC (polyvinyl chloride) plastic film, silicone rubber, stainless steel and office paper—is 0.432, 3.81, 5.86, 7.38 and 202 nm, respectively. In addition, the contact angles of a Bi<sub>35</sub>In<sub>48.6</sub>Sn<sub>16</sub>Zn<sub>0.4</sub> droplet on these five substrates, measured by means of a five-point fitting method with a contact angle meter (JC2000D3, Shanghai), are shown in figure 3. Each contact angle is the arithmetic average of five measured values. It can be seen that each contact angle is greatly influenced by the roughness of the substrate, which is in agreement with the results of Kramer <i>et al.</i> [36], whose research focus

![Figure 3](https://example.com/figure3.png)

Figure 3. Contact angles of a Bi<sub>35</sub>In<sub>48.6</sub>Sn<sub>16</sub>Zn<sub>0.4</sub> droplet on five substrates with different RMS roughness values. Five scatter points represent (from left to right) mica plate, PVC plastic film, silicone rubber, stainless steel and office paper. Inset presents an illustration of the contact angle between the droplet and the substrate. Error bars represent the standard deviation of the mean. (Online version in colour.)
Figure 4. (a) The conductive tracks written by a Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ filled heating pen on the PVC plastic film substrate. Panels (b) and (c) are, respectively, ESEM images of the width and thickness of the tracks shown in (a). (Online version in colour.)

is the wettability between gallium–indium alloy droplets and thin metal films. Among the five contact angle values, the contact angle between Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ and the office paper is the greatest, which indicates the poor wettability of Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ on office paper. By contrast, the contact angle between Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ and the mica plate substrate is the smallest, which is due to the smooth surface of the mica plate. However, there will be scratches on the mica plate when printing on it, because mica plate is thin and brittle. The contact angles between Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ and silicone rubber, PVC plastic film and the stainless steel are between the two extremes and are similar to each other. These three substrates can all have traces written on them. However, as the heating pen is fixed on a liquid metal printer [35] to provide accurate printing, the PVC plastic film performed better as the substrate than stainless steel and silicone rubber. The reason for this is that the stainless-steel plate cannot be bent and moved freely, and the thin (0.1–0.5 mm) silicone rubber is not manufactured as A4 paper size. PVC plastic films, purchased from Shanghai Yuanhao Office Equipment Co., Ltd, China, are used as the printing substrate in this article to perform the fabrication of patterns.

(b) Fabrication of conductive patterns and circuits

Figure 4a shows the printing tracks directly written with the liquid metal ink Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$. The environmental scanning electron microscope (ESEM) images of the width and thickness of the track are shown in figure 4b and 4c, respectively. The scrims on the surface
of the printed tracks are caused by the cold contraction of the liquid metal ink when it was cooled to the solid state from liquid. It can be seen that the measured width and thickness of the track are, respectively, 109.3 and 57.7 μm, which are much smaller than previous studies [21,23]. Undoubtedly, a higher resolution can be realized if a finer pen nib is used.

When the heating pen is held on a liquid metal printer, the location of the pen can be accurately controlled and complex patterns can be directly printed out. A sailing ship shape conductive pattern thus made is presented in figure 5a, which indicates the feasibility of drawing with liquid metal ink. In addition, the printed circuit on PVC plastic film substrate as shown in figure 5b can also be realized. Rapid manufacturing of circuits via this direct-write method may bring a revolutionary change to the current PCB manufacturing. A prominent problem that needs to be solved is the effective connection between the component pins and the liquid metal ink.

(c) Characterization of the printed resistor and the double-diamond antenna

To illustrate the practical value of the present method, a printed resistor is shown in figure 6a. The total length of the printed line between the two endpoints is 0.495 m, and the value of
Figure 6. (a) A printed resistor on the PVC plastic film substrate (scale bar is 1 cm in length) and (b) the resistance–temperature curve of the printed resistor. (Online version in colour.)

this resistor is 14.43 Ω as measured by an LCR digital electric bridge at room temperature. The resistance-temperature curve of this printed resistor is shown in figure 6b. Generally speaking, the resistance value increases with increasing temperature. As the temperature becomes lower than approximately 47°C, the curve changes slightly. However, there is a steep change in the resistance value near the melting point of the liquid metal Bi35In48.6Sn16Zn0.4 ink. This is due to the phase change of the printed liquid metal line in this temperature range. As the temperature rises to become higher than the melting point of the metal ink, the resistance–temperature curve changes slightly again. Such a device, which should be called a phase change resistor, could be used in temperature control systems because of its evident thermal sensitivity characteristic.

Figure 7a shows a printed double-diamond antenna on a PVC plastic film substrate. Each side of the diamond is 30 mm and the line width is approximately 0.4 mm. The frequency response of the reflection coefficient of this antenna is measured with a network analyser (Agilent N5230A), compared with the simulated result using Ansoft HFSS, as shown in figure 7b. The measured resonant frequency is 2.47 GHz, while the simulated value is 2.5 GHz. The good agreement between the measured and simulated results indicates that the printed antenna works as predicted.

4. Discussion

Printing with the heating pen loaded with the metal ink Bi35In48.6Sn16Zn0.4 introduced in this article is an important supplement to the current direct-write technology. Various patterns and circuits can be directly printed in a short time. The electrical conductivity of the metal ink is important in printing devices or circuits. Adding small amounts or nanoparticles of high-conductivity metals is an effective way of improving the electrical conductivity. Wettability between the substrate and the metal ink plays a decisive role in successful printing. More substrates which can ‘match’ with the metal ink should be developed. The articles printed with the ink Bi35In48.6Sn16Zn0.4 do not have good flexibility since they remain in the solid state at room temperature. Therefore, this metal ink is more suitable to be written onto solid substrates to manufacture instant PCBs, which will be the focus of our future investigations. When cracks arise in the wires of the printed circuit after long-term use, one just needs to heat the circuit to above the melting point of the metal ink to bridge the cracks together. In addition, the articles fabricated with this direct-write technology are easy to recycle and cause almost no pollution. A comparison between recycling GaIn24.5 and Bi35In48.6Sn16Zn0.4 is shown in figure 8. It can be seen that the solid-state Bi35In48.6Sn16Zn0.4 ink can be easily peeled off, whereas the liquid-state GaIn24.5 ink cannot. One matter that has yet to be resolved when using GaIn24.5 is how to handle any unused
liquid metal on the substrate. This liquid metal sticks easily to one’s skin and may potentially cause health problems because the surface of Ga is easily oxidized, which improves the adhesion between Ga and other surfaces. However, with Bi$_3$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$, one can conveniently peel the metal traces off the substrate, collect them together and then put them in a heating container to melt. This recycling measure causes no pollution, and saves the metal ink.

**Figure 7.** (a) A direct-write double-diamond antenna on a PVC plastic film substrate. Scale bar is 30 mm. (b) Comparison between the simulated and the measured reflection coefficients of the printed antenna. (Online version in colour.)

**Figure 8.** Comparison between recycling (a) Ga$_{34.5}$In and (b) Bi$_3$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$. (Online version in colour.)
5. Conclusion

In summary, we have presented a method of directly printing solidified electronic circuits or devices with the low-melting-point alloy Bi$_{35}$In$_{48.6}$Sn$_{16}$Zn$_{0.4}$ as the ink and suggesting the best material as the printing substrate. For future reference, the viscosity–temperature, electrical conductivity–temperature and thermal expansion–temperature curves of the metal ink were measured. At this stage, the achieved size of the printing tracks is already much smaller than previous efforts. Overall, the solid-state patterns and circuits could be fabricated via this direct-write method in a short period of time. For practical illustration, a liquid metal resistor was printed with its resistance–temperature curve measured, which indicated that such a resistor has the potential to be used in a temperature control system. Furthermore, a double-diamond antenna was also manufactured and there was good agreement between the measured reflection coefficient and the simulated result. With merits such as no pollution, no requirement for encapsulation and easy recycling, the present method is expected to be very useful in a wide variety of emerging printed electronics areas.

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