Three-dimensional interconnect layers inkjet printed on plastic substrates using continuous-wave xenon light sintering

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Received July 23, 2018; accepted November 12, 2018; published online December 12, 2018

This paper reports on results demonstrating printed interconnect layers fabricated on the surface of three-dimensional (3D) plastic objects with low heat-resistance using omnidirectional inkjet (OIJ) 3D printing method in conjunction with continuous-wave xenon light sintering. The xenon light sintering was carried out by attaching a condenser lens to the OIJ printing apparatus. The combination of xenon light focused by a condenser lens and a long time exposure helped realize large energy densities of 100 J cm⁻², which are comparable to pulsed xenon light energy. The combination of OIJ and continuous-wave xenon light technologies allowed us to fabricate 3D interconnect layers having resistivities of 13.3 ± 0.8 Ω along the 3D shape of plastic substrates. Furthermore, we found that the low thermal conductivity of plastic substrates makes it possible to carry out continuous-wave xenon light sintering without requiring assistive heating of the substrate. © 2018 The Japan Society of Applied Physics

1. Introduction

Applying printing methods to the manufacture of electronic devices, known as “printed electronics” is expected to be a low-cost, next-generation mass production technology because of its high-speed processing over large areas with high material utilization. Printed electronics also has the potential for creating innovative thin or flexible devices, which cannot be realized using conventional vacuum manufacturing processes. Such innovative devices require a high degree of design innovation using curved surfaces effectively, but conventional rigid and flat electronic circuit boards restrict designs using new forms factors. One of the most promising attempts in printed electronics is the diversification of design realized by adhering thin film devices onto curved substrates. However, since the shape of the curved device which can be achieved by affixing a film is limited to a columnar shape or the like, a better alternative is to form functional materials directly on the outer surface or the inner surface of the existing 3D object having curved surfaces. Conventional direct forming techniques for 3D objects such as 3D-MID and aerosol jet deposition are not printing methods, so they have limitations in cost or processing speed.

Recently, new printing methods that can be applied to 3D objects were proposed: screen-pad printing, gravure offset printing, inkjet printing. Among them, inkjet printing has several advantages, such as high ink usage efficiency and being a non-contact process that digital and on-demand. When fabricating interconnect layers using inkjet printing, a dispersion of metal nanoparticles in a solvent is often used to obtain high conductivity. After printing, conductivity appears by heat treatment of the substrate (a process called sintering). Here, if the molded plastic objects existing around us can be used as the printing objects, the application range of these techniques becomes extremely large. However, typical heat treatment temperatures of commercially available metal nanoparticle inks (e.g. NPS-J, Harima Chemicals Group) are above 200°C, which is higher than the glass transition temperature of many plastic substrates. Therefore, it is difficult to perform heat treatment steps using a conventional furnace in most instances.

Accordingly, sintering methods have been proposed that use pulsed xenon light, infrared light, electrical current, infrared irradiation, and microwave radiation. In particular, the sintering methods that employ pulsed xenon light have been widely studied since they can complete the conventional thermal sintering processes in extremely short times of 10 ms or less. On the other hand, since the flatness of the substrate and the distance between the exposure lamp and the substrate are very important in the pulsed xenon light sintering step, the substrates were limited to flat surfaces.

Roshanghias et al. attempted to apply multiple sintering methods to 3D objects. As a result, they found that pulsed xenon light technique was the most suitable for sequential layer-by-layer printing processing steps, while laser technique was the most suitable for bulk post-processing steps. The former method is appropriate for prototyping through the formation of objects from layers using a 3D printer, but inappropriate for mass production. Also, the latter method requires a small laser spot (about 10 μm in diameter) that is scanned at low speeds, so it takes a very long time produce with large-scale circuits. As a result, either method is inferior in terms of productivity.

This paper proposes a new patterning method that employs continuous-wave xenon light sintering combined with omnidirectional inkjet printing technology in the fabrication of interconnect layers onto 3D objects. Continuous-wave xenon light has been studied for carbon nanotubes as an alternative to pulsed xenon light, but there have never been examples where 3D application of sintering for silver nanoparticle ink. This method demonstrates that 3D interconnect layers can be fabricated by effectively sintering silver nanoparticle inks printed onto the surfaces 3D plastic objects with low heat-resistance.

2. Experimental methods

2.1. Layer printing and sintering on planar sample surfaces

A planar sample test pattern was fabricated using OIJ printing [Fig. 1(a)] and continuous-wave xenon light sintering [Fig. 1(b)]. The test pattern was a square shape, 12 mm in...
length and 12 mm in width, and printing was performed by moving a single-nozzle inkjet printhead in a spiral motion from the outside to the inside. The scan pitch was 100 μm, scan velocity was 1 mm s\(^{-1}\), and inkjet drop ejection frequency was 10 Hz. After drying at 60 °C for 30 min, xenon light sintering was carried out on a hot plate. Xenon light was focused to a diameter of 2.5 mm by a condenser lens (KLQ-2.5, ASAHI SPECTRA), and a spiral scan was performed in the same manner. The hot plate was used to heat the substrate simultaneously with light exposure. The temperatures of the hot plate settings were 40 °C, 60 °C, 80 °C, 100 °C. A commercially available silver nanoparticle paste (NPS-1, Harima Chemicals Group) was used as the ink. A glass slide (S1112, MATSUNAMI GLASS), a plastic plate made of acrylonitrile butadiene styrene (ABS) (NABS-90-90-5, Misumi), and an acrylic plate (AF501, Misumi) were used as substrates. The thicknesses of the substrates were 1 mm for glass slide, 5 mm for ABS plastic plate, and 5 mm for an acrylic plate, respectively.

### 2.2. Layer printing and sintering on 3D objects

3D interconnect layers over the edge of the substrate were fabricated using OIJ printing technology [Fig. 2(a)] and continuous-wave xenon light sintering was subsequently carried out [Fig. 2(b)]. The printhead was set to position (1) and was moved upward to position (2) at a velocity of 1.67 mm s\(^{-1}\) while ejecting ink at a constant frequency. While moving from position (1) to position (2), the ink flies in the horizontal direction and adheres to the vertically-oriented substrate. After reaching position (2), the printhead was moved to position (3) via position (3) at a velocity of 5 mm s\(^{-1}\). After reaching position (4), the printhead was moved downward to position (5) at a velocity of 1.67 mm s\(^{-1}\). In all of moving sections, the ejection frequency of the inkjet was set to 100 Hz. After a single printing step, the substrate was dried at 60 °C for 30 min, and xenon light sintering was carried out at the same position. Light exposure was performed by moving the condenser lens along the same path as the printhead. The travel velocity was 0.167 mm s\(^{-1}\) in the linear section, and 0.5 mm s\(^{-1}\) in the curved section. In the sintering process, light exposure was performed on both sides of the substrate. The ink and the substrate were of the same types as those used for the planar sample test patterns.

### 2.3. Printing and sintering system

3D interconnect layers were formed using a newly developing system incorporating xenon light exposure in conjunction with an OIJ apparatus using a vertically-articulated robot. A photograph of the apparatus is shown in Fig. 3. The printing process is performed by an inkjet printhead unit attached to the tip of a 6-axis vertical articulated robot arm (FD-H5, DAIHEN). After the drying process, sintering is performed by irradiation of xenon light using a condensing lens (KLQ—2.5, ASAHI SPECTRA) attached to the tip of the robot. Xenon light is directed to condenser lens using optical fiber connected to the xenon light source (MAX—303, ASAHI SPECTRA), and is focused to a spot diameter of about 2.5 mm for irradiation of the sample. The power density of the visible light is specified as 40 W cm\(^{-2}\).

According to some studies on the pulsed xenon light sintering, the pulse duration time is between 0.5 and 20 ms, and the irradiated energy density is between 2 and 50 J m\(^{-2}\) (Table I). Since the power of the continuous-wave xenon light source used in this study was minimal, it was necessary to focus its light to increase the energy density. In addition, the exposure is performed for an extended time compared with pulse light exposure technology, so that the light energy of the exposure was increased to the same extent. For large areas, sintering was performed by scanning a focused spot. In this case, the light energy density at one point on the line through which the focused spot center passes is expressed as the product of the power density and exposure duration (τ)

$$E = P \cdot \tau = P \cdot \frac{\varphi}{v},$$

where \(E\) is the light energy density, \(P\) is the power density, \(\varphi\) is the diameter of spot, \(v\) is the scanning velocity. From Eq. (1), the duration and the light energy in the spiral scanning condition of this paper were estimated to be 2500 ms and 100 J cm\(^{-2}\), respectively. In other words, the exposure energy of continuous-wave xenon light in this paper is roughly equivalent to that of conventional pulsed xenon light exposure technology.

The OIJ system in this paper is controlled by a personal computer (PC) (Fig. 4). This system consists of three subsystems. The first is a 6-axis vertical articulated robot (FD—H5, DAIHEN) and the PC. The robot operates...
according to the position and speed set by teaching, and the operation timing in each step is controlled by a PC. The second subsystem is an inkjet printhead unit, piezo amplifier (PZDR—0.3P4A, MATSUSADA Precision), a function generator (AFG3021C, Tektronix), and a PC. Using the signal controlled by the PC as an external trigger, the function generator generates an arbitrary waveform pulse. The arbitrary waveform pulse is amplified by the piezo amplifier and input to the piezo element in the inkjet printhead unit to eject ink according to the movement of the robot. The third subsystem is made up of a condenser lens (KLQ—2.5, ASAHI SPECTRA), optical fiber, xenon light source (MAX—303, ASAHI SPECTRA), and PC. The shutter of the light source is controlled by the PC in order to perform light exposure linked with the movements of the robot.

2.4. Microscopic observations and electrical measurements

The surface of the conductive layer after sintering was observed with a laser microscope (OLS 4000, Olympus). For the planar sample test pattern, the sheet resistance was measured in 10 points in the two samples using a 4-point probe (RGE-12, NPS), and the volume resistivity was calculated from the film thickness. For the 3D interconnect layer, electrical resistance measurements were carried out six times for the two samples (Fig. 5), using the four-terminal sensing mode of a digital multimeter (DMM—4050, Tektronix). The length of the interconnect layers to be measured were 11 mm for the glass slides, 15 mm for the ABS plastic plate and the acrylic plate, because the voltage measurement terminal was positioned at a point 5 mm from the edge of the substrate.
3. Results and discussion

3.1. Planar sample layer test patterns

Figure 6 shows the volume resistivity calculated from the measured sheet resistance values from planar sample test patterns sintered with continuous-wave xenon light exposure. Figures 6(a)–6(e) are the results on glass slide, and show the temperature of the assistive heating by the hot plate, (a) no heating, (b) 40 °C, (c) 60 °C, (d) 80 °C, and (e) 100 °C. Figure 6(f) shows results from the ABS plastic plate, and 6(g) shows results from the acrylic plate, both of which do not use assistive heating. An average measured film thickness of 1.1 μm was used for calculation. For the glass slide, the interconnect layers were non-conductive with xenon light sintering or with assistive heating below 60 °C. Xenon light sintering with assistive heating above 80 °C gives rise to conductivity and the volume resistivity decreases to $10^2 \mu\Omega \text{cm}$ with assistive heating at 100 °C. For the ABS or plastic or acrylic plates, no assistive heating was required to achieve conductivity in the interconnect layers, and a low volume resistivity of $10^2 \mu\Omega \text{cm}$ was obtained only with xenon light sintering. We presume that this is caused by the low thermal conductivity of the plastic substrates. Heat generated by the light exposure may stay inside the substrate longer, since substrates with low thermal conductivity are known to retain thermal energy. Compared to glass, the thermal conductivity of the acrylic or ABS plastic plates is about 1/5, which implies that this effect has a similar result to assistive heating.

The surface conditions observed with a laser microscope are shown in Figs. 7(a)–7(g). Similar to Figs. 6 and 7(a)–7(e) also show results on glass substrates with (a) no heating, (b) 40 °C, (c) 60 °C, (d) 80 °C, (e) 100 °C, (f) an ABS plastic plate with no heating, and (g) an acrylic plate with no heating. Microcracks were observed in all samples, and there was no clear correlation between the existence of microcracks and the conductivity of the conductive layers. The cross-sectional images observed with a scanning electron microscope (SU8000, Hitachi High-Technologies) are shown in Figs. 7(h)–7(n). Figures 7(h)–7(l) show results on glass substrates with (h) no heating, (i) 40 °C, (j) 60 °C, (k) 80 °C, (l) 100 °C, (m) an ABS plastic plate with no heating, and (n) an enlarged image of (m). Samples showed in Figs. 7(h)–7(l) were obtained by cracking planar test patterns on the glass slides, and a sample showed in Figs. 7(m)–7(n) was obtained by cutting 3D interconnect layers on the edge of ABS substrate. In Fig. 7(l), the presence of sintered silver having a bi-layer structure indicates that sintering progressed from the upper end and the lower end of the film, respectively. On the other hand, the ABS shown in Figs. 7(m)–7(n) does not have a layer structure inside the silver film like a glass substrate. This suggests that the silver ink on an ABS substrate is uniformly sintered with only light.

3.2. 3D interconnect layers

Figure 8 shows results of laser microscope measurements for the 3D interconnect layer sintered with continuous-wave xenon light, for Fig. 8(a) a glass slide, (b) an ABS plastic...
plate, (c) an acrylic plate, with (d) showing cross-sectional shape of interconnect layer on a glass slide, with (e) showing a cross-sectional shape of interconnect layer on an ABS plastic plate, and (f) the cross-sectional shape of interconnect layer on the acrylic plate. No obvious discontinuities were observed in Fig. 8(a) the glass slide, and Fig. 8(d) the height of interconnect layer was 1–3 μm. Large cracks were observed in Fig. 8(b) the ABS plastic plate, and in Fig. 8(e) the cross-sectional shape of interconnect layer was a concave shape of about 60 μm at its maximum depth. No large cracks were observed in Fig. 8(c) the acrylic plate, but in Fig. 8(f) the cross-sectional shape of interconnect layer nearly flat and its thickness could not be measured.

In terms of electrical measurements, Fig. 8(a) the glass slide and Fig. 8(b) the ABS plastic plate were non-conductive due to discontinuities in their interconnect layers, and in Fig. 8(c) a resistance value of 13.3 ± 0.8 Ω was obtained for the interconnect layer on the acrylic plate. Since the glass slide in Fig. 8(a) did not employ assistive heating for the planar sample test patterns, sufficiently conductive layers could not be obtained. For Fig. 8(b), it was presumed that the conductivity of the ABS plastic plate existed from the volume resistivity of the planar sample test pattern, but that large cracks were the cause of the discontinuities. These large cracks were caused by stress due to the concave deformation observed in the xenon light-sintered substrate. For the acrylic plate in Fig. 8(c), xenon light sintering had progressed sufficiently and large cracks did not occur, so that good conductivity was obtained. The cross-sectional shape of interconnect layer after xenon light sintering in the acrylic plate was almost flat, most likely because the substrate deformation seen in ABS plastic plate occurred on a small scale and became a concave shape having the same depth as interconnect layer thickness. The depth of the concave shape after sintering will depend on the difference in light absorption by the substrate. Since the wavelengths included in the
xenon light are distributed around visible light, the ABS plastic plate is opaque to the visible light and absorbs more of the light than the acrylic plate, which is transparent to the visible light. This suggests that the light causes greater thermal deformation for the ABS plastic plate.

4. Conclusions

These results demonstrate that 3D interconnect layers can be fabricated on the surface of plastic objects by combining OIJ printing and a continuous-wave xenon light sintering. Xenon light sintering was carried out by attaching a condenser lens to OIJ printing apparatus. Focused xenon light using a condenser lens and long continuous-wave exposure times realized large energy densities of 100 J cm$^{-2}$ almost equal to a pulsed xenon light energy. This method made it possible to fabricate a 3D interconnect layer with an electrical resistance of 13.3 $\Omega$ on an acrylic plastic object. The experimental results also implied that the low thermal conductivity of the plastic substrate does not require assistive heating and allows for sintering only with continuous-wave light. This method is expected to enable innovative devices with advanced designs that effectively utilize curved surfaces, by allowing for the fabrication of functional materials directly on the outer or inner surfaces of common 3D objects.

Acknowledgments

The vertically-articulated robot used in this research work was graciously provided by DAIHEN Corporation. This study was supported by the Japan Science and Technology Agency (JST) and JSPS KAKENHI Grant Number 16K13635.

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Fig. 8. (Color online) Results of laser microscope measurements for three-dimensional interconnect layers sintered with continuous-wave xenon light: glass slide, (b) ABS plastic plate, (c) acrylic plate, (d) cross-sectional shape of interconnect layer on glass slide, (e) cross-sectional shape of interconnect layer on ABS plastic plate, (f) cross-sectional shape of an interconnect layer on an acrylic plate.
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