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Highly Sensitive Antenna Using Inkjet Overprinting with Particle-Free Conductive Inks

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Supporting Information

ABSTRACT: Printed antennas with low signal losses and fast response in high-frequency bands have been required. Here we reported on highly sensitive antennas using additive patterning of particle-free metallo-organic decomposition silver inks. Inkjet overprinting of metallo-organic decomposition inks onto copper foil and silver nanowire line produced antenna with mirror surfaces. As a result, the overprinted antennas decreased their return losses at 0.5−4.0 GHz and increased the speed of data communication in WiFi network.

KEYWORDS: *inkjet printing, metallo-organic decomposition ink, silver nanowires, scattering parameters, antenna*

INTRODUCTION

A myriad of future electronic devices such as flexible smart phones, bendable displays, foldable lighting, and stretchable batteries are just about to be realized by inkjet printing with conductive inks.[1−4] An additive patterning made with inkjet printing is a practical facility in the fabrication of electronic devices. It has already been industrially applied in color filters for liquid crystal displays and has made significant contributions in increasing display sizes and decreasing production costs.[5] Additional advantages of inkjet printing are mask-less and noncontact printing. Mask-less printing allows the tracing of complicated device patterns and the modification of their designs from batch to batch. The absence of physical contact between the inkjet head and substrate allows the implementation of conductive lines on rough curved surfaces or pressure-sensitive surfaces.[3] Therefore, inkjet printing is one of the best technologies for the fabrication of printed electronics.

Antennas that transmit and receive high-frequency signals have comprehensive and diverse applications such as in smart phones, wireless network systems, automotive navigation systems, and radio frequency identification (RFID) tags. Because antennas are relatively simple structures compared with other electronic components such as transistors, they are easily fabricated using printing technology. Therefore, they are one of the most widely used devices in printed electronics and for high-speed data communication in high-frequency radios. However, in general, higher frequency radios have increased signal losses at the transmitter and receiver antenna. Consequently, the fabrication of antenna lines with low signal losses in the high frequency bands using printing technology remains a challenge. Here we report on highly sensitive antennas using additive patterning of particle-free metallo-organic decomposition (MOD) silver inks. The overprinted antennas achieved low signal losses over the megahertz to gigahertz ranges because of their surface smoothness as well as their thickness.

In our previous report, we succeeded in controlling a radio-controlled car remotely with a printed silver nanowire antenna on a plastic substrate.[6] Printed silver nanowire lines showed smaller return losses at 0.5−4.0 GHz compared with printed nanoparticle and flake lines, because of their smooth surface. Their high smoothness was obtained by incorporating tiny elements of silver nanowires with diameters of around 100 nm. Investigation of available conductive inks revealed some with infinitesimal elements for inkjet printing. One of them is an MOD ink, which does not contain solids. Instead of metallic nanoparticles, metallic precursor compounds of silver,[7,8] gold,[9] or copper,[10,11] are dissolved in organic solvents.

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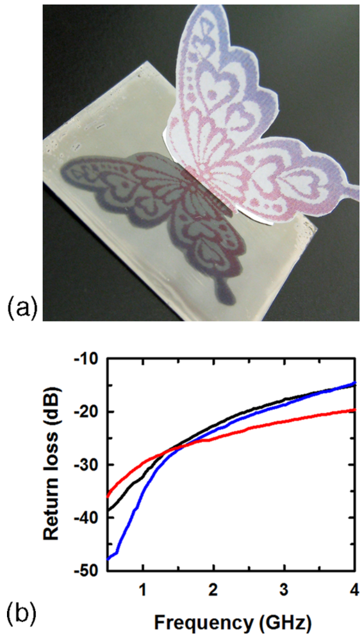

Figure 1. (a) Printed MOD film with a mirror surface. (b) Return losses of printed silver nanowire lines (blue), copper foil lines (black), and printed MOD lines (red).

EXPERIMENTAL SECTION

Materials and Antennas. Commercially available silver MOD inks (TEC-IJ-010, InkTec Co., Ltd., Korea) and silver nanowire pastes with ethylene glycol[6] were used in this study. Both printed conductors were heated at 100 °C for 30 min in air. Microstrip lines were fabricated using a base plastic substrate, which was patched with copper foils on both sides. The upper copper foil was 3 mm wide, 50 mm long, and 18 μm thick. When the return losses in the silver nanowire and MOD ink lines were evaluated, these conductors were printed on the microstrip lines on an area 3 mm wide and 10 mm long, where there were no patched copper foils (see Figure S1 in the Supporting Information). The MOD inks were overprinted onto the copper foil and silver nanowire lines on the microstrip line using an inkjet printer (Dimatix DMP 2831, Dimatix- Fujifilm Inc., USA), equipped with a 10 pL cartridge (DMC-11610). Printing conditions were set as voltage of 30 V and a frequency of 5 kHz using a customized waveform. The sample was maintained at room temperature during printing; the distance between the substrate and nozzle was set to 1 mm, and the dot spacing was set at 20 μm.

High-Frequency Characteristics. The return losses of conductive lines on a microstrip line were evaluated in an electromagnetic shielding bag using a network analyzer at 0.5−4.0 GHz (E5061A, Agilent Technologies Inc., Santa Clara, CA, USA, see Figure S2 in the Supporting Information). Their resistivity was measured using the four-point probe method (MCP-T610 Loresta type, Mitsubishi Chemical Analytech Co., Ltd.).

The resonance peaks of the inverted F antenna and overprinted antennas were evaluated in an electromagnetic shielding bag using a network analyzer at 0.5−4.0 GHz (E5061A, Agilent Technologies Inc., see Figure S3 in the Supporting Information). The modified antennas were deposited on the client adapter and then connected to a personal computer to perform the Internet access test using a WiFi network. Download speed tests were also performed by downloading some files of 10−350 MB size from the same Web site using the same WiFi network.

RESULT AND DISCUSSION

When the MOD inks were heated, metallic precursors were thermally decomposed, and metallic nanoclusters then emerged on the substrates. The development of the clusters led to highly conductive metallic thin films, which exhibited very smooth and bright shiny surfaces resembling a mirror (Figure 1a). The surface roughness was only 0.34 μm, which was less than half that of silver nanowire lines (0.76 μm) (Table 1). Furthermore, the resistivity of the thin film wires at 6.7 $\mu\Omega$ cm was as low as that for copper foil. The S11 parameter of return loss indicates a loss of signal power resulting from the reflection of the signal in a conductive line. When the antenna efficiently radiates, most of the incident power is radiated into free space, only a little of power reflected, called to return loss, which is measured as S 11.

Table 1. Characteristics of Silver Nanowire Lines, Copper Foils, MOD lines, MOD Overprinted Copper Foils, and MOD Overprinted Silver Nanowire Lines

	resistivity ($\mu\Omega$ cm)	surface roughness (Ra) (μm)	thickness (μm)
silver nanowire lines	70.5	0.76	6.0
copper foils	2.0	2.48	18.2
MOD lines	6.7	0.34	1.0
MOD overprinted copper foils	2.1	0.40	19.1
MOD overprinted nanowire lines	68.3	0.32	6.6

Because of their highly smooth surface and high conductivity, MOD lines exhibited small return losses less than −20 dB at 0.5−4.0 GHz (Figure 1b). In contrast, the return losses of silver nanowire lines and copper foils exceeded −20 dB at 2.5−4.0 GHz. Antennas for high-speed data communication in these bands benefit more from MOD lines than do silver nanowire lines and copper foils. However, at 0.5−1.5 GHz, the return losses for MOD lines were larger than those for silver nanowire lines and copper foils. These frequency bands are used for data communication via mobile phones and TV broadcasting. Therefore, it is necessary to reduce the return loss of MOD lines to be appropriate in antennas for these devices.

Large return losses at these bands were mainly caused by the "skin effect", which is the tendency of an electric current to become distributed within a conductor such that the current density is largest near the surface of the conductor.[12] The skin depth in the MOD lines, in which 65% of the current density is concentrated, was estimated from their resistivity values. The skin depths at 0.5 and 1.5 GHz were 6 and 3 μm. In contrast, the thickness of the MOD lines was around 1 μm because of their small silver loading (15 wt %). Therefore, thicker printed lines kept smooth surfaces will have improved their return losses.

Thicker printed lines can be easily fabricated using inkjet printing with MOD inks. For example, increasing the concentration or viscosity of inks would increase the thickness of the printed lines.[13,14] However, increasing their concentrations is not practical because of the poor solubility of the metallic precursors in organic solvents. Another approach to increasing the thickness of the lines involves controlling the wettability of the printed substrates.[15,16] Although the surface energy in the substrates was controlled appropriately, the thickness of the printed lines increased to twice or three times Because the thickness of the inkjet-printed lines was less than 1 μm, the wettability controlled thickness could not reach the required line thickness of 3−6 μm. Therefore, we concluded that the MOD inks should be inkjet overprinted onto a thicker conductive antenna with a rough surface, which resembles a surface finisher used to brush up its surface.

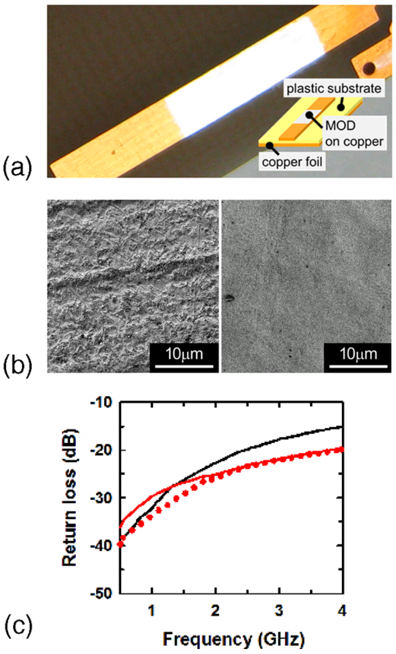

Figure 2. (a) MOD overprinted copper foil on a micro stripe line. (b) Surface FE-SEM image of a copper foil (left) and an MOD overprinted line (right). (c) Return losses in copper foil lines (black), MOD overprinted copper foils (dotted line), and MOD lines (red).

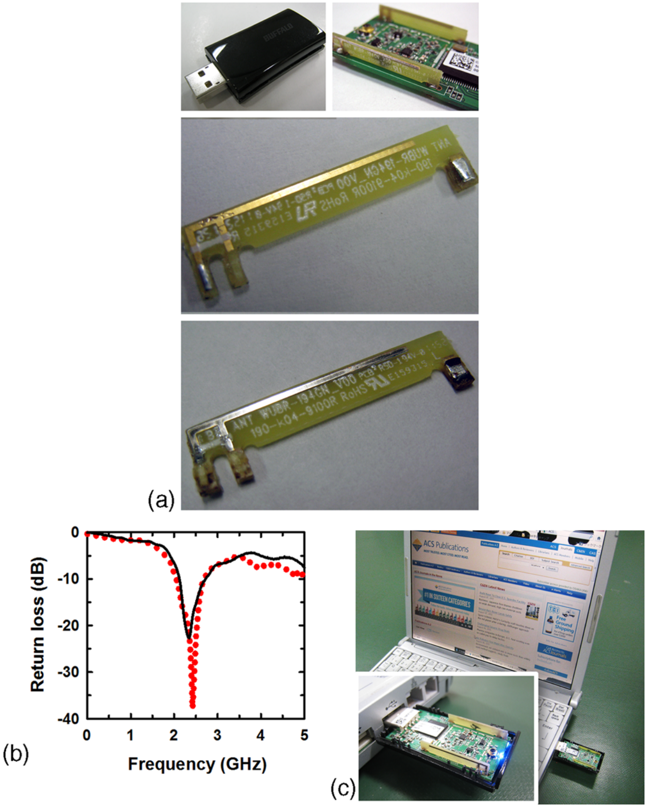

Figure 3. (a) USB wireless LAN client adapter (upper left), a client adapter without a cabinet (upper right), an inverted F copper foil antenna on plastic substrate (middle), and an MOD overprinted inverted F antenna on plastic substrate (lower). (b) Return losses for an inverted F copper foil antenna (solid line) and an MOD overprinted antenna (dotted line) (c) Demonstration of Internet Web page access via the modified client adapter with the overprinted inverted F antenna.

To improve surface smoothness, we inkjet overprinted copper foils with the silver MOD inks (Figure 2a). The silver MOD inks were accurately traced on their shapes without splashing, spreading, or repelling. Single overprinting of the MOD inks onto the copper foils removed rugged patterns from their surfaces (Figure 2b), decreasing the surface roughness (Ra) from 2.48 to 0.4 μm (Table 1). On the other hand, the thickness and resistivity of the overprinted copper foils were almost the same as those before overprinting (Table 1) because of the thinness of the overprinting layer at around 1 μm.

The larger return losses at 0.5−1.5 GHz in the MOD lines were because of their thickness of only 1 μm. On the basis of the skin depth, these frequency bands required a thickness of at least 3−6 μm. In contrast, the MOD overprinted copper foils had a 19.1 μm thickness with a small surface roughness of only 0.4 μm and a high resistivity of 2.1 $\mu\Omega$ cm. As a result, their return losses at 0.5 GHz were as small as those of the copper foils, and their return losses over 2.5 GHz were as small as those of the MOD lines (Figure 2c). In summary, overprinting onto copper foils with the MOD inks resulted in thick and low-resistivity lines with smooth surfaces, and the resulting antennas exhibited low loss of signal power at 0.5−4.0 GHz.

The silver MOD inks allowed precise additive patterning using inkjet printing and a highly smooth surface under low-temperature heating. Considering these advantages, overprinting with MOD inks onto manufactured antenna devices would improve their performance. A commercially available wireless LAN client adapter was used as an antenna device (Figure 3a). Wireless LAN client adapters enable computers and other devices to connect to existing wireless networks. In this device, an inverted F copper foil antenna of 1 mm wide was deposited onto the plastic substrates. Inverted F copper foil antenna is increasingly used in the mobile phone market due to good high-frequency characteristics and radiation performance. When the MOD inks was overprinted onto an inverted F antenna, the complicated patterns were completely traced and their surfaces became smooth (Figure 3a). The overprinted inverted F antenna exhibited a sharp resonance peak at around 2.5 GHz (Figure 3b). Note that the resonance point decreased from −22.7 to −37.7 dB because their surface roughness decreased from 0.42 to 0.27 μm using the overprinting with MOD inks. Smaller resonance points indicated a smaller signal power loss, which resulted from the reflection of the signal in the conductive lines.

Heat sintering for the MOD inks was sufficient at 100 °C for 30 min. Such low-temperature sintering leads to no or less damage to thermally sensitive plastic substrates, organic components, wiring, and bonding. Therefore, the modified client adapter with an overprinted inverted F antenna successfully transmitted and received signals over WiFi networks, enabling a personal computer to display a webpage (Figure 3c). Furthermore, the modified adapter increased the speed of data communication compared with the normal adapter because of their small resonance points. For example, the modified adapter took 7 s to download a 10 MB data file, whereas the normal adaptor took 8 s under the same network conditions. This increase in data volume decreased the download time drastically. When a high volume data file of 350 MB was downloaded, the download time decreased from 413 s using the normal adapter to 365 s using the modified adaptor. Therefore, by overprinting onto the antenna with only MOD inks, high-speed data communication was realized without the need to increase the capability of memory or CPU processors in computers or the power of transmitted signals.

As shown in Figure 1b, at 0.5−1.5 GHz, the silver nanowire lines showed return losses smaller than those of the MOD lines, whereas at 1.5−4.0 GHz, the return losses were greater than those of MOD lines. Consequently, inkjet overprinting with MOD inks was applied to the silver nanowire lines to decrease their large return losses at 1.5−4.0 GHz, as was the case with copper foils. Printed silver nanowire lines consisted of random networks with silver nanowires of 100 nm diameter and 5−10 μm long. Because there were numerous submicrometer-sized cavities inside and on the surface of the lines (Figure 4c), the silver nanowire lines appeared to be unpolished and dull gray (Figure 4a). When the MOD inks were inkjet overprinted onto the lines and then heated, their cavities on the surfaces were diminished and their surfaces were covered with silver thin films (Figure 4c). Moreover, they appeared to have a polished metallic surface (Figure 4b). Consequently, the surface roughness of the silver nanowire lines decreased from 0.76 to 0.32 μm (Table 1). The thickness and resistivity of the overprinted silver nanowire lines were 6.6 μm and 68.3 $\mu\Omega$cm, which were almost equal to the values before coating because of their thin silver coatings. As a result, the return losses under 1.0 GHz for MOD over printed silver nanowire lines were as small as those of the nanowire lines, and their return losses over 1.0 GHz were smaller than those of the MOD lines (Figure 4d). When the return losses of the overprinted silver nanowire lines were compared with those of the overprinted copper foils (Figures 2c and 4d), the overprinted silver nanowire lines exhibited smaller return losses for all frequency ranges. These results suggested that an MOD overprinted silver nanowire line was the most desirable antenna for high-speed data communication in high-frequency radios.

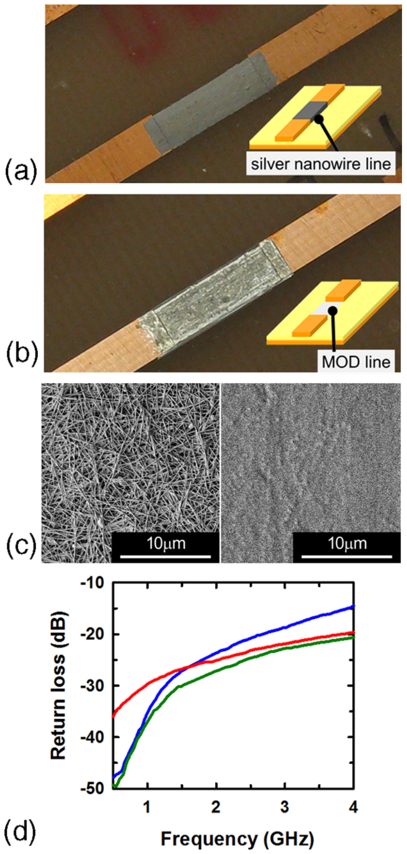

Figure 4. (a) Silver nanowire line on a micro stripe line. (b) MOD overprinted silver nanowire line on a micro stripe line. (c) Surface FE-SEM image of a silver nanowire line (left) and an MOD overprinted line (right). (d) Return losses in silver nanowire lines (blue), MOD overprinted silver nanowire lines (green), and MOD lines (red).

CONCLUSION

In summary, inkjet overprinting of MOD inks onto antenna patterns improved antenna performance. When the MOD inks were overprinted onto copper foils and silver nanowire lines, their surface became highly smooth and shiny bright. Such smooth surfaces enhanced the small signal losses over the megahertz to gigahertz ranges. In particular, the overprinted silver nanowire antenna exhibited the smallest signal losses. In the near future, our proposed process will be expected to be applicable to highly sensitive antennas in high-speed data communication applications for smart phones, wireless network systems, automotive navigation systems, and RFID tags.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

RFID, Radio Frequency IDentification; MOD, metallo-organic decomposition; LAN, local area network; WiFi, wireless fidelity; CPU, central processing unit; USB, universal serial bus

REFERENCES

(1) Gans, B. J.; Duineveld, P. C.; Schubert, U. S. *Adv. Mater.* **2004**, *16* (3), 203−213.

(2) Chabinyc, M. L.; Wong, W. S.; Arias, A. C.; Ready, S.; Lujan, R. A.; Daniel, J. H.; Krusor, B.; Apte, R. B.; Salleo, A.; Street, R. A. *Proc. IEEE* **2005**, *93* (8), 1491−1499.

(3) Junfeng, M.; Lovell, M. R.; Mickle, M. H. *IEEE Trans. Electron. Packag. Manufact.* **2005**, *28*, 265−273.

(4) Singh, M.; Haverinen, H. M.; Dhagat, P.; Jabbour, G. E. *Adv. Mater.* **2010**, *22* (6), 673−685.

(5) Ohta, T. *J. Surf. Finish. Soc. Jap.* **2009**, *60* (7), 431−434.

(6) Komoda, N.; Nogi, M.; Suganuma, K.; Kohno, K.; Akiyama, Y.; Otsuka, K. *Nanoscale* **2012**, *4*, 3148−3153.

(7) Vest, R. W.; Tweedell, E. P.; Buchanan, R. C. *Int. J. Hybrid Microelectron.* **1983**, *6*, 261.

(8) Teng, K. F.; Vest, R. W. *IEEE Trans. Compon. Hybrids Manuf. Technol.* **1987**, *12*, 545.

(9) Wehner, M.; Legewie, F.; Theisen, B.; Beyer, E. *Appl. Surf. Sci.* **1996**, *106*, 406.

(10) Hong, C. M.; Wagner, S. *IEEE Electron Device Lett.* **2000**, *21*, 384.

(11) Cuk, S.; Troian, M.; Hong, C. M.; Wagner, S. *Appl. Phys. Lett.* **2000**, *77*, 2063.

(12) Merilampi, S. L.; Bjorninen, T.; Vuorimaki, A.; Ukkonen, L.; Ruuskanen, P.; Sydanheimo, L. *Proc. IEEE* **2010**, *98* (9), 1610−1619.

(13) Kim, D.; Jeong, S.; Park, B. K.; Moon, J. *Appl. Phys. Lett.* **2006**, *89*, 264101.

(14) Kim, C.; Nogi, M.; Suganuma, K. *J. Micromech. Microeng.* **2012**, *22*, 035016.

(15) Osch, T. H. J.; Perelaer, J.; Laat, A. W. M.; Schubert, U. S. *Adv. Mater.* **2008**, *20* (2), 343−345.

(16) Kim, C.; Nogi, M.; Suganuma, K.; Yamato, Y. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2168−2173.