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Hybrid Stacked RFID Antenna Coil Fabricated by Ink Jet Printing of Catalyst with Self-assembled Polyelectrolytes and Electroless Plating

Chung-Wei Wang, Ming-Huan Yang, Yuh-Zheng Lee and Kevin Cheng
DTC/Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China
E-mail: wangcw@itri.org.tw

Abstract. *This article describes a method of forming a stacked hybrid metal structure and pattern to enhance radio-frequency identification antenna coil inductance. The essential strategies included the use of multilayer self-assembled polyelectrolytes to modify the surface property of substrates, an ink jet printing process for a Pd containing catalyst, and a stacked hybrid metal layer formed by electroless plating in subsequent processes. The results demonstrate that the minimum line width and line spacing can reach 100 μm/100 μm, and electrical performance is compared to prior research in employing different approaches. The method presented in this article enhances the capability by adapting to any substrate surface using the self-assembled polyelectrolyte technique. Therefore, results were verified on different substrates, such as PI, PET, and FR-4; satisfactory electric performance for application was obtained. In detail, the inductance of the antenna improved from 300 nH to 20 μH for a monolayer coil, and 600 nH to 50 μH for a double layer coil, depending on the metal thickness. © 2007 Society for Imaging Science and Technology.*
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INTRODUCTION

In recent years, printed organic electronics have been intensively developed because of their advantages of low cost, easy and flexible processing, efficient usage of material, and large scale manufacturing compared to conventional lithography and vacuum processes. These applications[1] include polymer light-emitting diodes (PLED), organic thin-film transistors (OTFT), organic bistable memory (OBD), metal circuits, etc. According to the forecast data from marketing research institutes, printed logic integrated circuits (ICs) will gradually attract more attention and will dominate in the future.[1] Among the logic ICs, radio-frequency identification (RFID) tags seem to be one of the most promising vehicles. These low cost printed products can replace not only bar codes but also expensive inorganic RFID silicon chips used for supply chain and automated retail checking. Generally, a simple RFID system (Figure 1) consists of a reader and a tag. There are many active and passive devices in a tag, including, at the least, an antenna, a capacitor, a diode, a transistor, and some memory. The system can be operated at lower frequencies, such as 125 kHz, 13.56 MHz, or 860−930 MHz, and at a higher speed of 2.45 GHz for different applications. Many companies have focused on printed RFID development with organic semiconductors; however, the operation frequency of these RFIDs is limited due to the low carrier mobility characteristic of organic semiconductors. Hence, a highly conductive coil for the tag antenna is necessary.[2,3]

At present, most tag antennas with good conductivity are fabricated by copper or aluminum etching. The line width and line space are 600−800 μm and 200−400 μm, respectively, in each common etching case. Metal paste consisting of silver can be used in screen printing or ink jet printing processes but suffers from low resolution, poor adhesion, and high cost. In addition, the resulting metal paste patterns always need a thermal curing process to sinter the metal particles in order to achieve acceptable conductivity. The curing temperature increases with silver particle size, and it represents a challenge for application to flexible substrates,[3,4] especially with the screen process.

Besides the issue of conductivity, high Q value inductors and well behaved capacitors are also required for power coupling and communication. High Q inductors can be achieved via several methods, which include adding magnetic material to the coil, increasing the number of circles, and reducing the resistance of the antenna coil. Among those measures, the addition of magnetic material is the best method for enhancing Q value.[4,5]

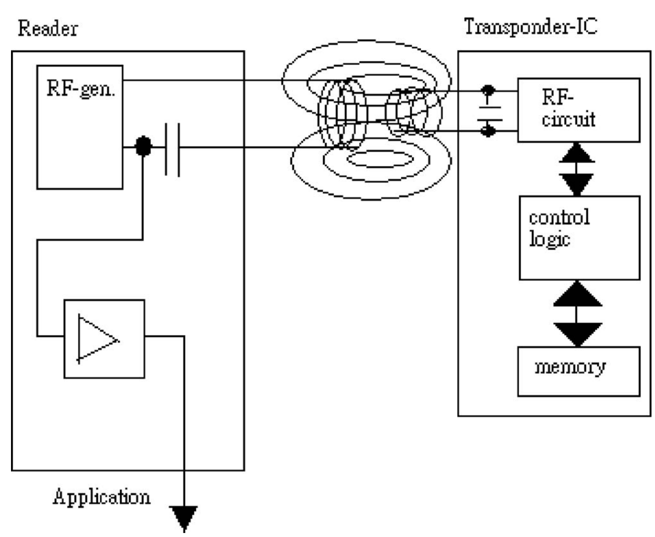

Figure 1. An RFID system.

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Because of the need for high inductance value, in this article, a hybrid circuit fabrication method combined with magnetic nickel layering onto an ink jet printed copper RFID antenna coil is presented. In this approach, the inductance of the antenna coil can be enhanced from 300 nH to 20 μH for monolayer cases, and from 600 nH to 55 μH for double-layer cases. We will discuss the details below.

EXPERIMENTAL

Chemical Preparation

Poly(allyamine hydrochloride) (PAH) (MW=55,000–65,000) and poly(acrylic acid) (PAA) (MW=70,000, 25% aqueous solution) were purchased from Aldrich. All chemicals were used without further purification. Deionized water (DI) was used in all aqueous solutions and rinsing procedures. The concentration of the polyelectrolyte-dipping solutions was 10 mM, based on the molecular weight (MW) of the repeat unit. The pH values of the PAH solution and PAA solution were adjusted to 7.5 and 3.5 by the addition of 1 M HCl and 1 M NaOH, respectively. Layer-by-layer assembly was carried out using an autodipping system. Before the layer-by-layer assembly process, double layer substrates were drilled to afford via holes to connect the two separated antenna circuits on each substrate side.

Ink Formulation and Pd-Catalyst Patterning

The catalyst ink was prepared by dissolving a Pd complex compound in DI water. The ink viscosity and surface tension were about $8-20$ cps and 40 dyne/cm, respectively. The printing process was conducted on a third generation print platform, designed and integrated for 550 mm $\times$650 mm substrates by the Industrial Technology Research Institute, Taiwan (ITRI). Polyimide (PI), polyethylene terephthalate (PET), and FR-4 substrates with different self-assembly layers were printed with the catalyst solution. While the solution was drying, the catalyst would be adsorbed on the substrate surface and would gradually diffuse into the layer of poly(allylamine hydrochloride) beneath; therefore, an ink jet defined area was afforded.[6–8]

Electroless Plating of Nickel

After the Pd-containing catalyst was patterned on the self-assembled polyelectrolyte layer, a commercial formulation, consisting of 40 g/L nickel sulfate, 20 g/L sodium citrate, 10 g/L lactic acid, and 1 g/L dimethylaminobenzaldehyde (DMAB) in DI water, for the electroless nickel plating, was used to further exchange the Ni with the Pd, and leaves the Ni at the location of the predetermined pattern. The optimum condition to obtain complete transport between Ni and Pd corresponds to pH 6.8, as determined by titration with 0.3 M ammonium hydroxide solution. Before deposition of nickel metal, the substrate needed to be dipped into the accelerator solution for about $3-10$ s and then washed with DI water and dried. In order to keep the solution homogeneous, an air bubble generator was used in the plating bath.[6–8]

Electroless Plating of Copper

A pure Ni circuit has good magnetic characteristics but is weak in terms of electronic performance, i.e., resistivity. We therefore explore how a combined layer of Cu with Ni, in a certain thickness ratio, may incorporate both the desired electrical and magnetic performance. Accordingly, we tried growing a copper layer on the Ni layer by the solution process. Theoretically, nickel and nickel plating solutions would induce copper ion reduction; the substrate with a nickel antenna coil, obtained from the previous plating process, then needs to be washed with DI water for 10 min to remove nonadsorbed nickel particles and nickel plating solution from the surface, and then dried prior to electroless plating of copper. All of the reagents for copper electroless plating were dissolved in DI water at room temperature with stirring. To keep the solution homogeneous, an air bubble generator was also used in the electroless plating bath; the pH value of which was controlled. The copper deposition was carried out at 40°C. Immersion time and temperature are two key factors with which to control the metal thickness. After being removed from the electroless plating solution, the samples were rinsed with DI water to remove residual plating solution and then set aside to dry. The structures of monolayer and double layer antenna coil are shown in Figure 2.[7,8]

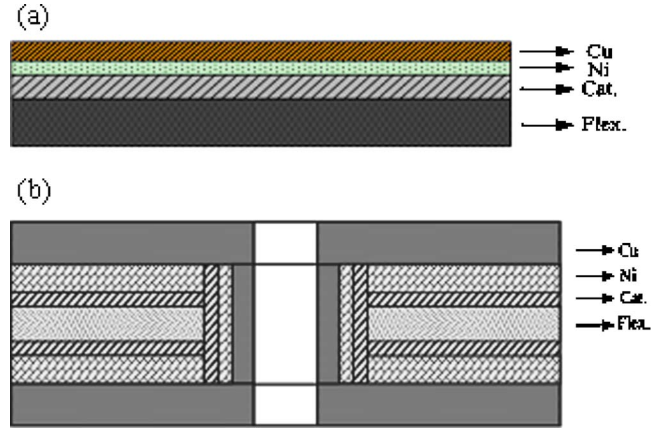

Figure 2. Schematic structures of the (a) single side antenna coil and (b) double side antenna coil.

RESULTS AND DISCUSSION

Table I lists the surface treatment processes to form self-assembled polyelectrolyte layers on a substrate. The repeating step for PAH/PAA bilayer deposition depends on the substrate. From our experience, for example, the PET substrate needs three repeats. Similarly, if this surface treatment is applied to the polyimide substrate, the number of repeating steps increases to seven. An antenna coil pattern with a line width of $75-100$ μm and line space of $75-100$ μm, was accordingly obtained. The resulting conductance can be adjusted by varying the nickel and copper electroless plating recipes. The edge of a nickel line of 2 μm thickness was uniform, as shown in Figures 3(a)–3(c). The line edge after electroless copper plating was still smooth, as shown in Figs. 3(d) and 3(e), where the copper metal thickness was 5 μm. The ratio of Ni film to Cu film is ~0.4 (2 μm/5 μm), which is determined by the resistivity and inductance. How-

Table I. Process flow of self-assembled polyelectrolyte layers before ink jet printing of catalyst.

Step	Condition
Substrate cleaning	Washing with toluene and DI-water in sequence
Immerse into $PAH_{(aq)}$	$PAH_{(aq)}$ (10 mM)
Substrate flushing	DI-water
Immerse into $PAA_{(aq)}$	$PAA_{(aq)}$ (10 mM)
Repeating (PAH/PAA) bilayer deposition	Up to three pairs of PAH /PAA layers
Immerse into $PAH_{(aq)}$ (10 mM)	$PAH_{(aq)}$ (10 mM)

ever, many unexpected particles were present within the line spaces [Fig. 3(f)], possibly from unwanted residual nickel particles and the nickel electroless solution. To measure the electrical characteristics, an RLC meter (Agilent 4294A) was employed, and the data thus recorded are shown in Table II. Table II indicated that adding Ni will dramatically increase the inductances, the L- and the Q-factor, but not reduce the resistivity. The inductances of monolayer hybrid RFID antenna coils (samples A and B) were about 50 times higher than that of the copper antenna coil (sample C), although the resistances were similar in both cases. The inductances of the double layer hybrid RFID antenna coils (samples D and E) were also ~90 times higher than for the double layer copper coil, in spite of the resistance of a double layer hybrid metal antenna being higher than that of the double layer copper by 12 Ω.

The measured deposition rates for electroless nickel and copper were 12 μm for 60 min and 5 μm for 60 min, respectively. In practice, the deposition rates were dependent on temperature, metal ion concentration, pH value of the bath solution, catalyst concentration, activator, the bath stability, and finally by electroless deposition time. In this study, the electroless bath stability was very important, because it influenced both the deposition speed and quality. The maximum thickness of nickel, which can be formed is up to 35 μm for over 3 h, and copper can be deposited up to 20 μm over 4 h. Compared to the results of Shan et al.,[8] who were able to deposit 5 μm over 1 h at saturation, this study made an obvious improvement in both growing rate and circuit performance. Accordingly, we changed the formulation for electroless plating, and have an activator process prior to electroless plating. We adopt the mist activator for 5−10 sec to coat a thin layer of activator on catalyst in order to speed up the reaction with electroless plating.

The incorporation of magnetic metal into the coil structure can dramatically enhance the inductance and the Q factor. The maximum Q factor, near 0.62, was achieved from a hybrid metal structure of 2 μm nickel and 5 μm copper in a single side antenna coil structure. A Q factor near 1.35 was achieved for the double side antenna, which is about double than that obtained in the single side case. The conductivity of the printed antennas was 90% and 80% that of bulk copper for the single side antenna and double side antenna, respectively. The higher resistivity was due to the impurities imbedded in the antenna coil by the electroless plating process. Hence, the Q factor could be further improved by resistivity reduction of the plating metal.

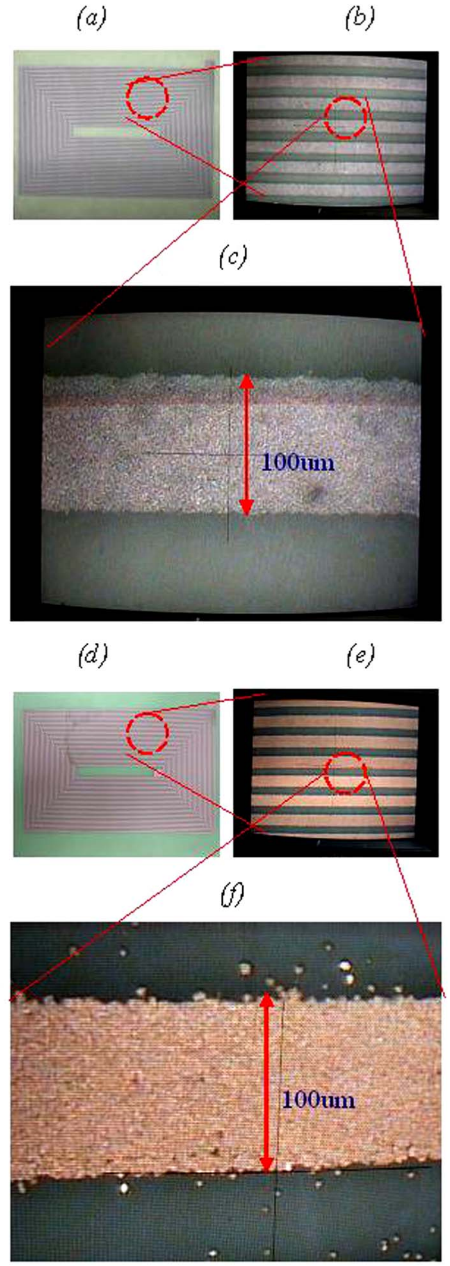

Figure 3. (a) and (d) are 100 μm wide printed single side antenna coil structure (27 circles layout); (b), (c), (d), and (f) are optical micrographs of printed inductor formed on commercial flexible substrates.

In addition to the Q factor, the impedance between antenna coil and interconnected coaxial cable should be about 50 Ω, on the basis of the layout of Fig. 1, in order to get the desired communication response of the single side circuit and double side circuit RFID antenna coils, as presented in Table II. The resulting impedance values were 29 Ω and 49 Ω for the single side antenna and double side RFID an-

Table II. Characteristics of the printed antenna coils in single side and double side circuits.

Sample	L (μH)	R_{ac} (Ω)	Q	Impedance (Ω)	Impedance phase (°)	R_{dc} (Ω)	Conductivity (s/m) Cu
Single side circuit A (2 μm Ni+5 μm Cu)	**16**	**21.1081**	**0.62**	**24.5845**	**32.2368**	**20.45**	**0.904**
Single side circuit B (2 μm Ni+5 μm Cu)	**17**	**25.8908**	**0.54**	**29.2636**	**27.3605**	**24.33**	**0.767**
Single side circuit C (only 5 μm Cu)	**0.3**	**23.3501**	**0.0093**	**N/A**	**N/A**	**N/A**	**N/A**
Double sides circuit D (2 μm Ni+5 μm Cu)	**55**	**40.1211**	**1.1**	**48.1572**	**40.2387**	**40.78**	**0.828**
Double sides circuit E (2 μm Ni+5 μm Cu)	**48**	**44.1578**	**0.96**	**50.3541**	**38.2173**	**42.35**	**0.758**
Double sides circuit F (Only 5 μm Cu)	**0.6**	**28.5872**	**0.02**	**N/A**	**N/A**	**N/A**	**N/A**

Figure 4. Photograph of the peeling test performed on the single side antenna with 3M TM-650 tape.

tennas, respectively. Obviously, a double side antenna with this design is more suitable than the single side antenna for use in RFID application. Furthermore, the double-side design can reduce the substrate size and signal interference attributed to the dense single side coil architecture.

The adhesion of this printed flexible RFID hybrid antenna coil was tested using 3M tape (TM–650). As shown in Figure 4, no observed peels proved that excellent adhesion between antenna coil and flexible substrate is achieved.[6]

CONCLUSIONS

We have successfully demonstrated that monolayer and double-layer RFID antenna coils can be manufactured by the use of multilayer SAMs, ink jet printing, and electroless plating processes. Incorporation of the magnetic metal nickel could dramatically enhance the inductance value and therefore the Q value. We can employ a multilayer antenna to obtain higher inductance with respect to the requirements for different layout designs. The resulting antenna coil is flexible and passes the 3M tape peeling test for PI, PET, and FR-4 substrates. The inductance of this antenna is improved from 300 nH to 20 μH for the single side coil, and 600 nH to 50 μH for double side coil, compared to the pure copper coil under the same conditions. Also, we found that the electroless plating recipes used for nickel and copper leads to side reactions, which resulted in impurities left in the coil, and led to a slight elevation of resistivity, which we expect to be able to change in the near future.

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