Asian Journal of Chemistry; Vol. 26, No. 6 (2014), 1565-1567

ASIAN JOURNAL OF CHEMISTRY

<http://dx.doi.org/10.14233/ajchem.2014.17289>

Formation of Hybrid Magnetic Films Composed of Fe_3O_4 and Epoxy Resin by Inkjet Printing†

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Published online: 10 March 2014;

AJC-14831

Hybrid magnetic films composed of Fe_3O_4 powders and epoxy resin were fabricated by inkjet printing process. Through the optimization of Fe_3O_4 ink and inkjet parameters, the Fe_3O_4 films were formed with the thickness from 5 to 100 μm . The film thickness could be adjusted by varying the solid content of Fe_3O_4 ink and repeating the number of inkjet printing of the Fe_3O_4 ink. To obtain a rigid magnetic film, epoxy resin was infiltrated into the Fe_3O_4 film and subsequently cured at 250 $^\circ\text{C}$. It was confirmed that highly-packed Fe_3O_4 hybrid film could be formed without any macro-voids after epoxy resin infiltration. The magnetic permeability and loss of hybrid Fe_3O_4 films with different film thickness were measured and those values at 13.56 MHz were compared. Magnetic properties of inkjet-printed Fe_3O_4 hybrid film was improved as the film thickness increased. Magnetic permeability and loss of Fe_3O_4 hybrid film with 30 μm thickness were 9.9 and 5.9, respectively.

Keywords: Inkjet, Fe_3O_4 , Hybrid, Permeability, Near field communication.

INTRODUCTION

Bulk magnetite (Fe_3O_4) shows significant values of spin polarization with a high Curie temperature of 858 K^{1-3} . It has been widely used in numerous applications such as microwave devices and magnetic devices^{4,5}. Fe_3O_4 -based magnetic films can be prepared by various techniques such as wet chemical coating, spin coating, liquid phase epitaxy, plasma spray and sputtering process⁴. Wet chemical coating is a simple process because the magnetic films are easily obtained by only immersing a substrate in the aqueous solution at moderate temperature. However, wet chemical coating process is sometimes limited to fabricate an electronic device because it is difficult to make a fine patterned-magnetic film for various applications.

Recently, inkjet process is an attractive technique in the fields of microelectronics due to its low consumption of source material and direct patterning process on various substrates^{6,7}. Especially, bottom up assembly of nanostructures and micro-electronic devices can be easily progressed by inkjet process through the accurate control of surface forces of small liquid droplets on heterogeneous surface^{8,9}. There have been many reports for inkjet-printed silver electrode for various applications, but the only few results were shown.

In this work, we tried to extend the use of inkjet printing to hybrid magnetic film formation for near field communication (NFC). According to the advances in wireless short range communication technology based on RFID technology, near field communication has been receiving a great attention lately in the market of mobile phone^{10,11}. The development of electro-magnetic noise suppressor made by the magnetic material with high permeability is essential for near field communication. Although the sintered ferrites were widely used for EMI shielding in electronic devices, the limitation of its application to mobile devices is still existed due to their high manufacturing temperature. Adding a resin component into the magnetic film, hybrid magnetic films could be prepared by Inkjet printing process at the relatively low temperature compared to conventional sintering process.

Hybrid magnetic films were prepared by inkjet printing of Fe_3O_4 powder ink and subsequent infiltration of epoxy resin ink. After the curing epoxy resin at 250 $^\circ\text{C}$, a rigid body of hybrid magnetic film could be formed. Magnetic permeability of inkjet-printed hybrid Fe_3O_4 films was discussed in detail monitoring the change of their microstructures.

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

EXPERIMENTAL

To make a magnetic ink, Fe_3O_4 powders were prepared with the diameter below 500 nm by mechanical milling process. Fe_3O_4 inks were formulated using organic solvent such as ethoxy ethanol and octanol. The Fe_3O_4 solid content in the solvent was fixed at 4–8 vol % in all experiments. In order to disperse the Fe_3O_4 powders in the solvent, they were mixed in the solvent by 24 h ball-mill process. The high speed mixing at 2,000 rpm was implemented for 8 min. The formulated Fe_3O_4 inks were filtered through a 6 μm nylon mesh before they were used to remove agglomerated powders in the inks. Omni-200 inkjet-printing unit (Unijet) was used in the experiment. Inkjet printing of magnetite ink was progressed by piezoelectric nozzle with 50 μm orifice. The distance between nozzle and substrate was maintained at 1 mm. The volume of ink droplet was fixed at 155–165 pl throughout the entire experiment. The ink ejection speed was 2.5–3.5 m/s. The printing frequency, substrate temperature and pitch between ink drops were modulated to fabricate a uniform Fe_3O_4 films on glass plates and polyimide films. Polyimide film was used as a substrate in the form of donut pattern to measure the magnetic property.

To obtain a highly-packed magnetite film, the solid contents of powders was maximized in ink formulation process and pitch size of inkjet-printed line was carefully controlled. After the magnetite film formation, resin infiltration into magnetite film and curing was progressed to make a rigid body at 250 $^{\circ}\text{C}$ for 2 h. The roughness and thickness of the inkjet-printed ferrite films were measured by a Veeco Dektak 150 surface profiler. The microstructure of the inkjet-printed films was looked at by focused-ion-beam field emission scanning electron microscope (FIB FE-SEM; Nova 200). The magnetic permeability and loss in the frequency region of 1–3 GHz were obtained by measuring the impedance of the samples using an RF impedance/material analyzer (Agilent E4991A).

RESULTS AND DISCUSSION

The Fe_3O_4 ink was printed as various test patterns, to evaluate the printing accuracies and optimize the process parameters. The printing experiments were performed on glass and polyimide film substrates simultaneously. Fig. 1 shows the distribution of the Fe_3O_4 powders after both dot and line patterns were dropped and dried on the glass plates. The dot pattern showed the ring patterned accumulation of Fe_3O_4 powders on the surface. In the central region of the droplet, a little coverage of Fe_3O_4 powders was observed. The height of the Fe_3O_4 ring was *ca.* 4 μm while the thickness of the center area was below 1 μm . The inkjet-printed line with the Fe_3O_4 ink in Fig. 1(b) showed the accumulation of Fe_3O_4 powders at both sides of the line. The outward flow in the Fe_3O_4 droplet moved most of the powders to the sides of the line. The accumulation region at the side of line pattern after a fast drying of solvent in Fe_3O_4 ink system showed a high packing density of Fe_3O_4 powders compared to central region. To obtain a magnetic film with high permeability and low magnetic loss, a highly-packed microstructure is essential. Therefore, the overlapping concept of highly-packed region in the inkjet-printed line pattern was employed to make a high performance magnetic film.

Fig. 1. SEM image and surface profile of inkjet-printed Fe_3O_4 ink (a) drop, (b) line

Fig. 2 is the inkjet-printed Fe_3O_4 line varying the pitch size. It is observed that the continuous lines began to form at the pitches from near 100–50 μm . However, when the pitch reduced to less than 50 μm , bulges were observed along the printed line. These bulges are a commonly observed in the inkjet printing process, especially at relatively small ink-droplet pitches. Therefore, basic printing condition of Fe_3O_4 ink could be obtained through the evaluation of Fe_3O_4 droplet on the substrates.

Fig. 2. Inkjet-printed Fe_3O_4 lines with different ink-droplet pitches: (a) ink-droplet pitch at 200 μm , (b) 150 μm and (c) 100 μm (continuous line) and (d) 50 μm (bulges)

Considering the properties and the parameters of Fe_3O_4 inkjet-printed lines, Fe_3O_4 films were printed out on glass substrates by overlapping the printed lines together. Since there was non-uniform accumulation of Fe_3O_4 powders on the lines, the line-to-line pitch was kept similar to the accumulation width in the individual line, 38.1 μm as shown in Fig. 3. The concept of line overlapping was also shown in Fig. 3. Through applying the line-to-line pitch of 38.1 μm , uniform Fe_3O_4 film could be formed without any depletion region. Actual printing image of Fe_3O_4 film formation was also shown by capturing the CCD image. When the Fe_3O_4 film with 10 μm thickness was formed, the roughness was about 0.5 μm . The thickness of the Fe_3O_4 film could be increased by repeating the inkjet-printing of the Fe_3O_4 film. It could be also adjusted by varying the content of Fe_3O_4 powders in the ink. The optimum solid content of our Fe_3O_4 ink system was 4 vol % considering its printing parameters.

Fig. 4(a–b) show the surface morphology and the cross-sectional image of the inkjet-printed Fe_3O_4 film, respectively. In the as-printed Fe_3O_4 film, there were no cracks and macro-

Fig. 3. CCD image of the inkjet-printed Fe_3O_4 film surface with octanol single solvent system. The line-to-line pitch was adjusted to the same value as the width of the coffee ring of $38 \mu\text{m}$

defects on the whole surface as shown in Fig. 4 (a). However, it was observed that there were a large number of voids after packing the Fe_3O_4 powders by inkjet printing in the cross-sectional image in Fig. 4(b). The air gap between the Fe_3O_4 particles deteriorates the magnetic properties suppressing the generation of magnetic flux.

Fig. 4. FE-SEM image of the inkjet-printed Fe_3O_4 film: (a) the surface morphology (b) the cross-section image

To remove the air component in the as-printed Fe_3O_4 film, the resin infiltration process was employed. After preparing the epoxy-based resin ink dissolved in ethylene glycol monoethyl ether acetate, the resin was printed on the Fe_3O_4 film. Due to the low viscosity, the epoxy-based resin was infiltrated well into the layer. Through the infiltration process, the microvoids inside the Fe_3O_4 film were fully filled with epoxy resin as shown in Fig. 5(a-b). In the magnified image in Fig. 5(b), it was confirmed that the epoxy resin covered the Fe_3O_4 powders and filled the empty space effectively.

Fig. 5. FE-SEM cross-sectional images of the resin-infiltrated Fe_3O_4 films fabricated by the inkjet-printing method. (a) low magnification image and (b) high magnification image

In order to investigate the optimum thickness of Fe_3O_4 films as a magnetic layer for near field communication, the inkjet-printed films with different film thickness from 12 to $30 \mu\text{m}$ were prepared. The magnetic permeability and loss of hybrid Fe_3O_4 films on donut patterned polyimide substrate with different film thickness were measured and those values at 13.56 MHz were compared. Table-1 showed that the magnetic permeability (μ') increases from 3.6 to 9.9 with increasing the thickness of Fe_3O_4 film from $12 \mu\text{m}$ up to $30 \mu\text{m}$. Over the same range of the thickness, on the other hand, the magnetic permeability loss (μ'') decreases from 9.8 to 5.2.

TABLE-1
MAGNETIC PERMEABILITY AND LOSS
OF INKJET-PRINTED Fe_3O_4 FILMS AT 13.56 MHz

	Thickness (μm)	Permeability	Magnetic loss
Inkjet-printed	12	3.6	9.8
hybrid Fe_3O_4	22	5.1	6.9
films	30	9.9	5.2

Conclusion

The Fe_3O_4 hybrid magnetic films were fabricated by inkjet printing. The pitch size of inkjet-printed Fe_3O_4 dot and line was optimized by monitoring the distribution of Fe_3O_4 powders. To maximize the packing density of Fe_3O_4 film, line pitch of $38 \mu\text{m}$ was maintained. After the formation of Fe_3O_4 film, epoxy resin was infiltrated into the film by inkjet printing. It was confirmed that epoxy resin covered the Fe_3O_4 powders well and filled the micro-voids effectively. Finally, hybrid magnetic film was fabricated in the rigid film by curing at 250°C . Hybrid film thickness was controlled from 12 to $30 \mu\text{m}$ and the surface roughness was *ca.* $0.5 \mu\text{m}$. Magnetic permeability and loss of Fe_3O_4 hybrid film with $30 \mu\text{m}$ film thickness was 9.9 and 5.2 at 13.56 MHz, respectively.

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