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Method for the fabrication of thick multilayered nickel/iron oxide nanoparticle magnetic nanocomposites

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ABSTRACT

Magnetic nanocomposites consisting of ferrite nanoparticles and magnetic metals have been of interest for use in power electronic components due to their ability to achieve relatively high magnetic permeabilities while also having low losses. Unfortunately, fabrication challenges limit the maximum achievable thickness of these films to $\sim 4 \,\mu m$, though thicker films are desirable for increased power handling. To overcome these challenges this works seeks to demonstrate a fabrication method whereby thick composite films can be made by constructing sequential composite layers, performing electrophoretic deposition and electro-infiltration steps for each layer. Composite samples of iron oxide nanoparticles electro-infiltrated with nickel that are 1, 3, 5, 7, and 10 layers thick will be fabricated and characterized both structurally and magnetically. Structural measurements accomplished with SEM show that each layer appears to contribute 4 µm to the total thickness, with the one layer sample being 3.99 ± 0.12 µm thick and the ten layer sample being 39.19 ± 3.1 µm thick. Results show that the dc magnetic properties of these composites stay constant as thickness increases, having an average magnetic saturation of 464 kA/m, and coercivity of 2.5 kA/m. The ac magnetic properties similarly showed that the permeability of the composites also stayed consistent at 20. However, the dimensional resonance frequency of the composites decreased as thickness increased, lowering to \sim 96 MHz for 1 layer (\sim 4 µm) to \sim 8 MHz for 10 layers (\sim 40 µm), revealing a trade-off between thickness of a maximum operating frequency.

1. Introduction

There has been an increased interest focused on miniaturizing onchip power components, such as inductors, to keep up with the continued decrease in the footprint of the overall size of power supplies and devices [14,16]. Currently, single phase materials such as ferrites and magnetic metal alloys are used for power components [12]. However, the intrinsically low magnetic saturation and low permeability of ferrites and the high loss of magnetic metal alloys inhibit the miniaturization of the single-phase materials for power supplies that are switched at high frequencies [6,12,14,16]. Magnetic nanocomposites that combine magnetic metal alloys and ferrites have the potential to improve a variety of on-chip components by simultaneously achieving high permeability and high magnetic saturation with low loss [6,13,18,19,21]. The degree of efficiency with which these magnetic nanocomposites operate as power components can be represented by the maximum of the material's power handling [12]. The relationship

between the power handling of a material and its dimensions, the operating frequency, and characteristic magnetic behavior can be seen in the following equation (Eq. (1))

$$P_{max} = \frac{V_{core} f_{SW} B_s^2}{2\mu} \tag{1}$$

where P_{max} is the maximum power handling, V_{core} is the volume of the core, f_{SW} is the switching frequency, B_s is magnetic saturation, and μ is the permeability (real component) of the core [17]. Fabricating nanocomposites from two magnetic materials such as ferrite nanoparticles and a magnetic metal alloy result in a high magnetic saturation (B_s) because of the presence of the magnetic metal alloy, while simultaneously keeping the losses of the overall composite low because of the electrically non-conductive ferrite nanoparticles. An increase in the magnetic saturation increases the P_{max}, but the magnetic metal alloy also increases the permeability (μ) , which will decrease the overall

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power handling (Eq. (1)). Ensuring that power handling remains high with this material system while also realizing a small footprint can therefore be achieved by increasing the overall thickness of the composites, which increases V_{core} .

The fabrication of magnetic nanocomposites in a way that is both compatible with semiconductor fabrication processes and can simultaneously possess high permeability and high magnetic saturation with low loss has been explored in work first developed by Wen et al. and Hayashi et al. using a method called electro-infiltration (EI) to create a magnetic metal matrix that surrounds a magnetic nanoparticle film [8,20,22]. In brief, magnetic nanoparticles were consolidated into a film onto a conductive substrate via drop-casting (Wen et al.,) or electrophoretic deposition (Hayashi et al.,). The magnetic nanoparticle film was then infiltrated with nickel or permalloy, filling in the pores of the film with a magnetic metal/metal alloy. While drop-casting is a simple and time-efficient method to form a consolidated nanoparticle film, it often leads to non-uniform and uncontrollable nanoparticle film thicknesses Li et al., [10]. To combat non-uniformity from dropcasting iron oxide nanoparticles, work from our group and others has utilized electrophoretic deposition (EPD) as the particle assembly method for magnetic nanocomposite fabrication [4,13]. EPD is colloidal technique that deposits charged particles in suspension under an applied, external electric field onto a conductive substrate [2]. Results from our work and others show that EPD is a reliable nanoparticle deposition method that can form porous films of magnetic nanoparticles that are thicker than those that are drop-casted, and that films deposited via EPD can be used in conjunction with EI to form magnetic nanocomposites [5,7,13,15]. It is also important to note that EPD is a method that can be readily integrated into batch manufacturing processes, making it a particularly attractive prospect for the fabrication of on-chip power components. However, experimentally there seems to be an inherent thickness maximum of $\sim 4\,\mu m$ to the EPD + EI process due to limitations of the infiltration process in which, after $4 \,\mu m$ of a nanoparticle film is infiltrated, the electroplated metal will plate a solid film of magnetic metal on top of the formed composite, rather than infiltrating the particles, pushing particles away from the formed composite [18]. This issue limits EI from achieving the very thick films that are required for high power handling.

Considering the thickness limitation that electro-infiltration presents, this work seeks to introduce and demonstrate a fabrication method whereby the EPD + EI process is used to deposit nanocomposite layers in 4 µm increments to overcome the 4 µm limitation of a single nanocomposite layer. Specifically, we will use EPD to deposit a film of iron oxide nanoparticles and use EI to infiltrate the deposited nanoparticle film with nickel up to 4 µm. These two steps will then be sequentially repeated until the final layer number is achieved. In order to demonstrate this process, as well as to understand what effect the number of layers has on the behavior of the resulting composite, we fabricate 1, 3, 5, 7, and 10 layered samples and investigate their structural, dc magnetic and ac magnetic properties. The results presented here show that each layer is approximately the same thickness, providing a method that could theoretically be carried on to realize as thick of a final composite as desired, and in a controllable manner. Furthermore, we find that the dc magnetic properties are consistent throughout all samples, regardless of layer number, while the ac magnetic properties show a constant permeability with a downward shift in maximum operating frequency as layer number increases. This indicates that while thickness will limit the maximum operating frequency of any device these composites are used within, it demonstrates that thicker composite cores can be achieved. Therefore, by using this semiconductor processing compatible fabrication method, it will allow for a higher maximum power handling than what was previously achievable.

2. Materials and Methods

2.1. Iron oxide nanoparticles

2.1.1. Synthesis

Iron oxide nanoparticles were synthesized via aqueous coprecipitation based on a previously established method [11]. Briefly, iron (II) and iron (III) chloride salts were combined in a molar ratio of 1:2, respectively, in an alkaline (pH 8–9) environment for one hour at 85 °C under nitrogen. After one hour, the particles were collected with a large permanent magnet, and were subsequently washed, and dialyzed to remove excess salts. After three days of dialysis with a water change at 4 h and then at 18-hour intervals after the first change, the particles were resuspended in water with the addition of tetraethylammonium hydroxide (TEAH). TEAH acts as a peptizing agent, creating a stable suspension of particles in water, which served as the stock solution for electrophoretic deposition with a concentration of 47 mg/mL.

2.1.2. Characterization

The physical size of the iron oxide nanoparticles was measured via transmission electron microscopy (TEM) using a 200 kV FEI TALOS F200I S/TEM. A dilute solution of particles was evaporated on a lacey carbon-mesh copper grid. ImageJ software (NIH) was used for size measurements (n = 250 measurements). The crystalline phase of the assynthesized iron oxide nanoparticles was verified with X-ray diffraction (XRD) using a Panalytical X'pert powder diffractometer. A Cu anode was used to supply Ka radiation, and a scintillation detector (45 kV, 45 mA) with a step size of 0.008°. The phase of the powder samples was confirmed via comparison to a reference magnetite (Fe₃O₄) diffraction pattern (98-004-4525 from the International Center for Diffraction Data (ICDD)). Scherrer's formula was used to calculate the average crystallite size (τ) via the equation, where k is the shape factor (assumed as 0.9 for spherical particles), λ is the X-ray wavelength (1.54 Å), β is the full width half maximum value for the peak of interest in radians (which has been corrected for instrument broadening), and θ is the Bragg angle, also in radians.

2.2. Magnetic nanocomposites (iron oxide nanoparticles/nickel)

Fig. 1a outlines the fabrication process for the multilayered composites (with layer numbers of 1, 3, 5, 7, and 10). The process first consists of the patterning of substrates with photoresist to form toroidal molds (8 mm outer diameter, 3.1 mm inner diameter) on silicon or aluminum foil-based substrates. An example of a fabricated toroidal sample can be seen in the stereomicroscope image in Fig. 1b. This sample geometry is necessary for measurement of the complex permeability of the multilayered materials using the Agilent 16454A Magnetic Material Test Head, which measures the sample as the core of a one-turn inductor. Electrophoretic deposition was used to deposit films of iron oxide nanoparticles into the toroidal molds on the substrates. These iron oxide nanoparticle films were then electro-infiltrated with nickel to form one layer of the iron oxide nanoparticle/nickel nanocomposite. To form subsequent layers of composite, the single layer composites were sonicated to remove any excess iron oxide nanoparticles after infiltration, and the electrophoretic deposition of iron oxide nanoparticles followed by the electro-infiltration of nickel steps were repeated. After the desired number of layers was achieved, the photoresist mold was removed with acetone, leaving the multilayered magnetic nanocomposite. The details of each step are provided below.

2.2.1. Substrate fabrication and patterning

Samples were fabricated on two different substrates, p-type $\langle 100\rangle$ silicon and $\sim 24~\mu m$ thick aluminum foil. Silicon wafers were used as a more traditional substrate on which power components would typically be fabricated. However, to measure the permeability of these materials, the samples were required to be cut into a toroidal shape, which is not



Fig. 1. Schematic overview of the multilayer nanocomposite fabrication process is shown in (a). Step 1 shows the sputtered gold surface of the substrate (silicon and titanium adhesion layer not shown) patterned with photoresist. Step 2 includes the electrophoretic deposition of iron oxide nanoparticles into the mold, followed by Step 3, the electro-infiltration of nickel throughout the iron oxide nanoparticle film. Steps 2 and 3 were repeated until the number of layers that were needed were achieved. Finally, Step 4 shows the removal of the photoresist mold, leaving the multilayered composite. A stereomicroscope image of particles in a toroidal mold with photoresist still around the mold is shown in the (b). Torroid samples were fabricated due to the shape of the Magnetic Material Test Head for complex permeability measurements.

possible on rigid silicon wafers. Therefore, aluminum foil was used as the other substrate material as it is easily cut into a toroidal shape for permeability measurements. The samples fabricated on silicon were used for characterization via vibration sample magnetometry (VSM), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). Aluminum foil served as the substrate for the permeability measurement samples. For both substrates, the fabrication steps were identical. First, a 20 nm thick titanium adhesion layer and a 100 nm thick gold seed layer were deposited on the substrate using sputter deposition (KJL CMS-18 Multi-Source Sputterer). Afterward, a \sim 10 μm thick layer of KMPR 1010 negative photoresist (from Kayaku Advanced Materials, Inc.) was deposited on the substrate using a spincoater at 3000 rpm. After the subsequent soft bake (5 min at 100 °C), exposure (670 mJ/cm² dose considering the gold layer and using a Karl Suss MA6 Mask Aligner), and post exposure bake (2 min at 100 °C), the resist was then developed for 2 min in SU-8 developer, rinsed, and blown dry with nitrogen. Special care was taken to keep the aluminum foil substrate from folding or creasing during fabrication.

2.2.2. Electrophoretic deposition of iron oxide nanoparticles

Iron oxide nanoparticles in the prepared stock solution were added to 0.01 M hydrochloric acid (HCl) in isopropanol (IPA) to form a one volume percent (1 vol%) solution for electrophoretic deposition, giving the particles a high, positive surface charge (zeta potential of \sim 30 mV). The zeta potential of dilute solutions of the iron oxide nanoparticles in water with pH values between 3 and 10 were measured with a Brookhaven ZetaPlus instrument. The positively charged particles in suspension are then able to move towards a negatively charged electrode, which in this case is the patterned substrate, under an applied external electric field. A positively charged electrode was connected to a graphite block and placed parallel to a substrate, connected to the negative

The two electrodes were placed 1.5 cm apart, with an electric field of 30 V/cm applied. EPD was carried out for 30 min, and the films were dried in air for 10 min prior to electro-infiltration. A summary of the experimental parameters for EPD is shown in Table 1.

electrode, via connections to a power supply (Bio-Rad PowerPac HV).

2.2.3. Electro-infiltration

After electrophoretic deposition the iron oxide nanoparticle films were dried in air. After drying, electro-infiltration was performed using a nickel sulfamate electroplating bath from Technic Inc. (Elevate Ni 5910 RTU). A 3.7x3.7 cm² nickel foil served as the anode, while the patterned substrate with the iron oxide nanoparticle film served as the cathode (with an anode to cathode spacing of 3.3 cm). A 5.4 cm³ neodymium-iron-boron (NdFeB) retaining magnetic was placed approximately 1 cm behind the substrate to hold the nanoparticles in place during infiltration. A benchtop power supply (Keithley 2400 SourceMeter) was used to supply a constant current density of 10 mA/cm², and the electro-infiltration process was performed at 54 °C for 20 min to achieve a ~ 4 μ m thick layer. Following electro-infiltration, the samples were rinsed with DI water, sonicated to remove any excess iron oxide nanoparticles, and dried with compressed air. These electro-infiltration parameters are summarized in Table 1.

2.2.4. Nanocomposite characterization

The thickness of the samples fabricated on p-type 100 silicon was measured via stylus profilometry using a Tencor Alpha-Step AS500 stylus profilometer. These measurements were carried out after the photoresist molds were removed with acetone. For samples fabricated on aluminum foil, the thickness was measured using cross-sectional SEM, performed with an FEI Nova SEM 430 at an accelerating voltage of 5 keV. Samples were cut in half and mounted on 45° stubs. After

Table 1

Parameters for electrophoretic deposition and electro-infiltration.

Electrophoretic deposition		Electro-infiltration	
Applied electric field	30 V/cm	Applied current density	10 mA/cm^2
Electrode spacing	1.5 cm	Cathode-anode spacing	3.3 cm
Particle concentration	1 vol%	Plating solution	Elevate Ni 5910 RTU
Solvent/[HCl]	IPA/0.01 M	Temperature	54 °C
Time	30 min	Time	20 min

tilting each sample between 45 and 60° to reveal the cross-section of the composite, 25 measurements were taken for each sample using four to five images. Image analysis was performed using ImageJ software, and measurements were averaged to determine the average thickness of the sample.

SEM using EDS was used to qualitatively confirm the formation of the multilayered magnetic nanocomposites. The samples fabricated on p-type 100 silicon were cleaved and the cross-sections were analyzed via SEM using the EDS capabilities included with the FEI Nova SEM. EDS was used to identify detectable concentrations of iron and nickel at an accelerating voltage of 15 keV. An even distribution of iron in nickel was used to confirm the successful infiltration of nickel within the iron oxide nanoparticle film for each layer of the composite. Additionally, SEM was used to image the surface morphology of the multilayered samples.

In order to determine that the film deposition of the multilayer samples on the silicon and aluminum foil substrates were comparable, a five layer sample on both substrate materials was measured with X-ray diffraction (XRD) using a Panalytical X'pert powder diffractometer. A Cu anode was used to supply K α radiation, and a scintillation detector (45 kV, 45 mA) with a step size of 0.008°. Additionally, an omega offset of 5° was employed to avoid damage to the detector from interacting with the $\langle 100 \rangle$ silicon substrate.

The dc room temperature magnetic behavior of an iron oxide nanoparticle film deposited via EPD, electroplated nickel film, and the multilayered magnetic nanocomposites was measured with an ADE Tech. EV-9 vibrating sample magnetometer (VSM). Magnetic fields between -1800 and 1800 kA/m were applied at room temperature, and the resulting magnetic hysteresis curves were obtained.

The complex permeability of the multilayered samples was measured using an Agilent E4991A RF Impedance/Material Analyzer with a 16454A Magnetic Material Test Fixture. The final toroidal samples were cut out using a hole punching tool and a pair of non-magnetic scissors. The real (μ ') and imaginary (μ ") parts of the complex permeability of these samples was calculated by $\mu' = 1 + (X_S - X_{air})/\mu_0 \cdot h \cdot \ln(b/a)$ and μ " = ($R_S - R_{air}$)/ $\mu_0 \cdot h \cdot \ln(b/a)$. Here, X_s is the imaginary part of the impedance when the sample is not in the test head, R_s is the real part of the impedance when the sample is in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the impedance when the sample is not in the test head, R_{air} is the real part of the toroid sample, b is outer radius of the toroid sample, and a is the inner radius of the toroid sample [3].

3. Results and Discussion

3.1. Iron oxide nanoparticles

An X-ray diffraction (XRD) pattern of the synthesized iron oxide nanoparticles is shown in Fig. 2a. The synthesized particles were compared to a magnetite (Fe₃O₄) reference pattern (98–004-4525) from the ICCD database. Peaks located at $2\theta = 30.4$, 35.7, 53.7, 57.3, and 63.0° can be attributed to the inverse spinel crystal structure that is expected from the magnetite phase of iron oxide (Fe₃O₄). The average crystallite size was calculated using Scherrer's formula using the following three 2θ values: 35.7, 57.3, and 63.0° . The as-synthesized particle crystallite size was calculated as 17.19 ± 2.2 nm. To compare to the crystallite size, the physical size of the nanoparticles was measured using images from transmission electron microscopy (TEM) with ImageJ (Fig. 2b). The physical size from TEM was 15.13 ± 3.0 nm, shown in the inset in Fig. 2b, which is in good agreement with the XRD data.

The room temperature magnetic behavior of the iron oxide nanoparticles after deposition via electrophoretic deposition (EPD) was measured with vibrating sample magnetometry (VSM). The hysteresis curve of the iron oxide nanoparticle film can be seen in Fig. 3, which shows a magnetic saturation (M_s) of 148 kA/m and a coercivity (H_c) of 1.7 kA/m. In comparison to the bulk Ms of magnetite nanoparticles, 340 kA/m, the film of deposited nanoparticles via EPD achieved approximately 44% of this bulk value. This decrease in the Ms of the nanoparticle film as compared to bulk magnetite nanoparticles is expected due to the porous nature of the films. These measurements are volume normalized, where the total volume is that of the particles and the pores between them. Overall, the M_s of iron oxide nanoparticles is lower when compared to bulk Fe₃O₄ due to surface spin disorder at the nanoparticle surface [9]. Additionally, the H_c, measured as 1.7 kA/m, which is relatively low, can be attributed to the existence of particle interactions within the film. The iron oxide nanoparticles then served as the ferrite inclusion phase, deposited via EPD, to be used in the subsequent multilayered magnetic nanocomposite fabrication.

3.2. Magnetic nanocomposites

After the multilayered composites were fabricated with EPD + EI, they were first cleaved for cross-sectional imaging via SEM to investigate the layer thicknesses, overall thickness, and distribution of iron oxide nanoparticles within the nickel matrix. Fig. 4 shows SEM cross-sectional



Fig. 2. X-ray diffraction (XRD) pattern (a) of the synthesized iron oxide nanoparticles compared to a reference magnetite (Fe_3O_4) patterned from the ICDD database (98–004-4525), shown in solid squares. A transmission electron microscopy (TEM) image (b) of the synthesized iron oxide nanoparticles. The distribution of sizes were measured via ImageJ (n = 250) and is shown in the top left corner of (b).



Fig. 3. Hysteresis curves of the multilayered magnetic nanocomposites (1, 3, 5, 7, and 10 layers) along with the constituent materials, nickel (Ni) and iron oxide nanoparticles (IONP). Inset in the bottom-right corner is a zoom-in to the center of the hysteresis curves. Both the magnetic saturations and coercivities of the multilayered nanocomposites fall between those of the constituent materials.

images along with EDS maps of the cross-sections of the one, three, five, seven, and ten layered iron oxide nanoparticle/nickel magnetic nanocomposites. For each sample, the distribution of iron (Fe) in the nickel



(Ni) matrix indicates that the infiltration of the iron oxide nanoparticle film with nickel has been successful, thus fabricating a magnetic nanocomposite. The thickness of the samples fabricated on a silicon substrate (Fig. 4) were measured via stylus profilometry, with the average roughness values reported as error, which can be found in Table 2. The thickness of the one-layer sample ($3.99 \mu m$), when multiplied by the number of layers of a sample, correlates well with the final thickness of the multilayered composite throughout the series of samples. This indicates consistent particle deposition via EPD and rate of infiltration with nickel with increasing number of layers. It is interesting to note that these distinct layers are observed in the final microstructure in the cross-sectional images (Fig. 4).

Additionally, it is worth noting that the thickness of each layered composite on the two different substrates yielded similar results, confirming similar deposition for each substrate type. XRD was utilized to compare a five layer sample deposited on silicon and aluminum foil to confirm that similar deposition on each substrate material was occurring. Supplementary Figure S1 shows the two diffraction patterns from the five layer samples on each substrate, showing similar peaks attributed to gold, from the surface of the substrate, and nickel from the sample itself. Due to the high intensity of several of the peaks and some amorphous signal at low 20, seen in the aluminum foil sample's diffraction pattern (Supplementary Figure S1), signal from the iron

 Table 2

 Thicknesses of samples fabricated on silicon wafer vs. aluminium foil substrates.

No. of layers	Silicon wafer (µm)	Aluminum foil (µm)
1	3.99 ± 0.12	5.19 ± 0.8
3	10.94 ± 1.5	11.79 ± 1.4
5	19.32 ± 3.1	18.16 ± 2.2
7	25.17 ± 3.1	26.70 ± 3.5
10	39.19 ± 3.1	34.79 ± 3.7



Fig. 4. Scanning electron microscopy (SEM) cross-sectional images with the corresponding energy dispersive X-ray spectroscopy (EDS) maps directly to the right of the SEM image for the 1, 3, 5, 7, and 10 layered composites (a-e, respectively), showing the iron oxide nanoparticles (seen via the iron (Fe) signal) well-dispersed in the nickel (Ni) matrix). SEM cross-sectional images also reveal distinct layers that correlate with the desired layer number of the particular sample. The average thickness (T) of each sample in a-e is shown in the bottom left corner of the respective SEM micrograph.

oxide nanoparticles is unable to be resolved. However, the XRD data does indicate that the nickel deposited via electro-infiltration is similar on both substrate materials.

One can additionally observe that there is a degree of non-uniformity in the overall thickness of the composites due to surface roughness. The surfaces of the one, five, and ten layered samples on silicon substrates were imaged via SEM, seen in Supplementary Figure S2. Although there are some visible differences in surface morphology within each sample, the SEM images of the three different samples do indicate minimal changes in the surface morphology as layers are added. To achieve a higher degree of uniformity in film thickness, mechanical polishing could be implemented to decrease the overall surface roughness of the composite film.

The dc magnetic behavior of the multilayered samples along with their two constituent materials (a film of iron oxide nanoparticle deposited via EPD and an electroplated nickel film), were measured via vibrating sample magnetometry (VSM), with the resulting M-H curves shown in Fig. 3. Each layered composite, consisting of 1, 3, 5, 7, and 10 layers, have an average saturation magnetization of 464 kA/m, which falls between the saturation magnetization values of the iron oxide nanoparticle film (148 kA/m) and the electroplated nickel film (540 kA/ m). Similarly, the average coercivity of the multilayered composites were measured at 2.5 kA/m, which falls between the coercivity of the nickel film (6.7 kA/m) and the iron oxide nanoparticle film (1.7 kA/m), seen in the inset in Fig. 3. These results show that the fabricated multilayered composites exhibit an averaging of the magnetic behavior of the two constituent materials rather than a superposition of the hysteresis curves. This averaging behavior has been suggested in previous work [13,18]. The similar saturation magnetization and coercivity values for each layer number shows that as layer number, and corresponding thickness, increases, the dc magnetic behavior of the composites does not change, which is to be expected as the materials themselves are expected to be identical regardless of thickness.

The real and imaginary parts of the permeability for the multilayer samples are shown in Fig. 5a and 5b, respectively. The real parts of the permeability show a common dc permeability of ~ 20 , estimated by taking the average value of the curves as they approach 1 MHz in Fig. 5a. In Fig. 5b, it is seen that the value of the resonance frequency shifts downward as the number of layers increase, going from ~ 96 MHz for 1 layer to ~ 8 MHz for 10 layers. This shift in the resonance frequency suggests that the observed resonance arises due to dimensional resonance, which decreases with increases in the cross-sectional area of a

sample [1]. This result suggests that there is a trade-off between the thickness of these magnetic materials (which contributes to high power handling) and the maximum operable frequency, which also contributes to a high power handling. The multilayered magnetic nanocomposites fabricated in this work, composed of layers of iron oxide nanoparticles surrounded by a nickel matrix, exhibit similar saturation magnetization (M_s) and permeability (μ) values regardless of layer number. This indicates that improved power handling is dependent on an increased core volume (via increased thickness) and operational frequency.

4. Conclusion

This work presents a method for the fabrication of multilayered magnetic nanocomposites via sequential electrophoretic deposition of iron oxide nanoparticles and infiltration of nickel into the porous iron oxide film to overcome the thickness limitation of electro-infiltration to ultimately improve magnetic power handling of the materials. The fabricated materials harness the increased magnetic saturation of magnetic nanocomposites composed of ferrite nanoparticles and magnetic metals while also achieving thicker films via the multilayered approach. The results shown here demonstrate the ability of the electrophoretic deposition and electro-infiltration method to be sequentially repeated to form multilayered magnetic composites to achieve thicker composites. Cross-sectional SEM images and EDS elemental maps show the dispersion of iron through a nickel matrix, indicating successful composite formation, as well as consistent layer thicknesses, signaling uniform deposition and infiltration rates for each layer. The saturation magnetizations and coercivities of the multilayered composites are an average the two constituent materials, which additionally shows successful composite fabrication, while the consistency in dc magnetic behavior across all multilayered samples shows no dependence on layer number. However, complex permeability measurements show that as layer number increases from one layer to ten layers, the resonance frequency shifts downward from \sim 96 MHz to \sim 8 MHz, respectively. This suggests that there is ultimately a trade-off between the ultimate thickness of the magnetic nanocomposites and the maximum operable frequency. Overall, this work provides a batch manufacturing method that is compatible with semiconductor fabrication to create thicker on-chip magnetic nanocomposites. Though the maximum operating frequency of any device these composites are used in will be limited by the thickness of the composite film, the fabrication process presented here has the capability to achieve higher maximum power handling than was



Fig. 5. Permeability plots for the 1, 3, 5, 7, and 10 layered iron oxide nanoparticle/nickel magnetic nanocomposites, specifically the (a) real (μ ') and (b) imaginary (μ '') permeability. Note that peak frequency on the imaginary permeability plot (b) for each layered sample shifts to lower frequency values as the layer number increases.

previously achievable. This method could additionally have broad applicability for material systems that require nanocomposites. Future work could involve addressing the thickness limitation of the electroinfiltration process to fabricate even thicker layers and investigating the downward shifting resonance peak in the imaginary permeability as thickness increases.

CRediT authorship contribution statement

Sara C. Mills: Conceptualization, Methodology, Validation, Writing – original draft, Visualization. Connor S. Smith: Writing – review & editing, Investigation, Validation. Sai Pranesh Amirisetti: Investigation, Writing – review & editing. Noah Ferson: Data collection. David P. Arnold: Supervision, Writing – review & editing. Jennifer S. Andrew: Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- R.E. Alley, A review of new magnetic phenomena, Bell System Tech. J. 32 (1953) 1155.
- [2] L. BESRA, M. LIU, A review on fundamentals and applications of electrophoretic deposition (EPD), Prog. Mater. Sci. 52 (1) (2007) 1–61.
- [3] R. Dosoudil, Determination of permeability from impedance measurement using vector network analyzer, JEE 63 (7) (2012) 97–101.
- [4] S. Kelly, X. Wen, D.P. Arnold, J.S. Andrew, Electrophoretic deposition of nickel zinc ferrite nanoparticles into microstructured patterns, AIP Adv. 6 (2016), 056105.

- [5] S.K. Kurinec, N. Okeke, S.K. Gupta, H. Zhang, T.D. Xiao, Synthesis and electrophoretic deposition of magnetic nickel ferrite nanoparticles, J. Mater. Sci. 41 (24) (2006) 8181–8185.
- [6] K. Gorecki, K. Detka, Influence of power losses in the inductor core on characteristics of selected dc-dc converters, Energies 12 (2019) 1991.
- [7] S. Hashi, S. Yabukami, A. Maeda, N. Takada, S. Yanase, Y. Okazaki, High-frequency magnetic properties of ferrite particulate films, J. Magn. Magn. Mater. 316 (2) (2007) 465–467.
- [8] Y. Hayashi, S. Hashi, K. Ishiyama, Magnetic properties of nanostructured film composed of co-ferrite nanoparticles and metal co prepared by combination of electrophoretic deposition and electroplating, IEEE Trans. Magn. 48 (11) (2012) 3170–3173.
- [9] H. Khurshid, W. Li, M.-H. Phan, P. Mukherjee, G. Hadjipanayis, Surface spin disorder and exchange-bias in hollow maghemite nanoparticles, Appl. Phys. Lett. 101 (2012), 022403.
- [10] H. Li, D. Buesen, R. Williams, J. Henig, S. Stapf, K. Mukherjee, E. Freier, W. Lubitz, M. Winkler, T. Happe, N. Plumere, Preventing the coffee-ring effect and aggregate sedimentation by in situ gelation of monodisperse materials, Chem. Sci. 9 (2018) 7596.
- [11] R. Massart, "Preparation of aqueous magnetic liquids in alkaline and acidic media", IEEE Trans, Magn. 17 (1981) 1247.
- [12] S. Mathuna, T. O'Donnell, N. Wang, K. Rinne, Magnetics on silicon: an enabling technology for power supply on chip, IEEE Trans Power Electron. 20 (2005) 585.
- [13] S.C. Mills, C.S. Smith, D.P. Arnold, J.S. Andrew, Electrophoretic deposition of iron oxide nanoparticles to achieve thick nickel/iron oxide nanocomposite films, AIP Adv. 10 (2020), 015308.
- [14] Y. Mai Nguyen, D. Bourrier, S. Charlot, Z. Valdez-Nava, V. Bley, C. Combettes, T. Lopez, J.-P. Laur, M. Brunet, Soft ferrite cores characterization for integrated micro-inductors, J. Micromech. Microeng. 24 (10) (2014) 104003, https://doi.org/ 10.1088/0960-1317/24/10/104003.
- [15] S.D. Oberdick, S.A. Majetich, Electrophoretic deposition of iron oxide nanoparticles on templates, J. Phys. Chem. C 117 (36) (2013) 18709–18718.
- [16] P.M. Raj, P. Chakraborti, H. Sharma, K. Han, S. Gandhi, S. Sitaraman, M. Swaminathan, R. Tummala, Tunable and miniturized RF components with nanocomposite and nanolayered dielectrics, Proc. 14th IEEE Int. Conf. Nano. (2014) 27–31.
- [17] P. Markondeya Raj, H. Sharma, S. Sitaraman, D. Mishra, R. Tummala, System scaling with nanostructured power and RF components, Proc. IEEE 105 (12) (2017) 2330–2346.
- [18] C.S. Smith, S. Savliwala, S.C. Mills, J.S. Andrew, C. Rinaldi, D.P. Arnold, Electroinfiltrated nickel/iron-oxide and permalloy/iron-oxide nanocomposites forintegrated power inductors, J Magn. Magn. Mater. 493 (2020), 165718.
- [19] C.R. Sullivan, D.V. Harburg, J. Qiu, C.G. Levey, D.i. Yao, Integrating magnetics for on-chip power: a perspective, IEEE Trans. Power Electron. 28 (9) (2013) 4342–4353.
- [20] X. Wen, J.D. Starr, J.S. Andrew, D.P. Arnold, Electro-infiltration: A method to form nanocomposite soft magnetic cores for integrated magnetic devices, J. Micromechanics Microengineering 24 (10) (2014) 107001, https://doi.org/ 10.1088/0960-1317/24/10/107001.
- [21] X. Wen, S.J. Kelly, J.S. Andrew, D.P. Arnold, Nickel-zinc ferrite/permalloy (Ni0.5Zn0.5Fe2O4/Ni-Fe) soft magnetic nanocomposites fabricated by electroinfiltration, AIP Adv. 6 (5) (2016) 056111, https://doi.org/10.1063/1.4943415.
- [22] X. Wen, J.S. Andrew, D.P. Arnold, Exchange-coupled hard magnetic Fe-Co/CoPt nanocomposite films fabricated by electro-infiltration, AIP Adv. 7 (5) (2017) 056225, https://doi.org/10.1063/1.4976951.