

Magnetic and Mechanical Properties of Micromachined Strontium Ferrite/Polyimide Composites

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Abstract—In this work, strontium ferrite/polyimide composite thin films are fabricated and characterized for micromachining applications. The application of these materials in microelectronics and micromachining dictates the use of different polymers than those previously used for conventional plastic magnets due to fabrication compatibility constraints. The material investigated here consists of magnetically anisotropic strontium ferrite particles suspended in a benzophenone tetracarboxylic dianhydride-oxydianiline/metaphenylene diamine polyimide matrix. Magnetic, mechanical, and processability properties of these composites are investigated for a strontium ferrite loading range of 55%–80% by volume. Intrinsic coercivity H_{ci} , residual magnetic flux density B_r , and maximum energy product $(BH)_{max}$ have been determined. For an 80% by-volume concentration loading of ferrite, H_{ci} of 318 kA/m, B_r approaching 0.3 T, and $(BH)_{max}$ of 11 900 T · A/m have been achieved. Biaxial Young's modulus and residual stress are determined using a slightly modified *in-situ* load/deflection technique. The biaxial Young's modulus increases with increasing the magnetic powder loading. The materials have been deposited and patterned using two techniques: 1) screen-printing and 2) spin-casting, followed by photolithography. Finally, a simple magnetic microactuator made with those materials has been fabricated and tested, which demonstrates the usefulness of those materials to micromachining. [243]

Index Terms—Composite, ferrite, magnetic microactuator, permanent magnet, polyimide.

I. INTRODUCTION

RECENTLY, there has been much interest in magnetic materials in microelectronics and micromachining, for applications such as integrated inductive components, electromagnetic interference shielding, and magnetic microactuators and microsensors. However, in many cases, materials which have suitable hard magnetic properties may not be compatible with standard microelectronics processes. For example, the preparation of samarium-cobalt and neodymium-iron-boron magnets usually requires high temperature, pressing, and sintering. Polymer magnets composed of polymer matrices and magnetic powder, although possessing inferior magnetic properties than cast or sintered magnets, have various advantages, e.g., higher manufacturability, possible production of com-

plicated small and thin shapes with precision, etc. Such polymer magnets have been widely used in various fields, e.g., electronic and communications instruments, household tools, and audio equipment. A number of papers and reviews on these polymer magnets have been published [2]–[6]. Based on this previous work, it appears that magnetic polymer composites are a good compromise to combine the favorable properties of the magnetic material with the simple processing sequences of the polymer. The purpose of this work is to investigate the suitability of these materials for micromachining applications.

In this work, a magnetic composite material compatible with standard microelectronics and micromachining processes is described and characterized. The characteristics of interest include the magnetic properties (intrinsic coercivity H_{ci} , residual magnetic flux density B_r , and maximum energy product $(BH)_{max}$), mechanical properties (Young's modulus and residual stress), and processability. The material properties of the composite films are evaluated for a strontium ferrite loading range of 50%–80% by volume. Then, a simple microactuator is presented to illustrate the applicability of polymer magnets to micromachining.

II. MATERIALS SELECTION

Since the composite consists of both a polymer matrix and a magnetic powder, suitable candidates for both components were investigated. The choice of the polymer matrix is based on the following factors: its ability to accept large-volume loadings of magnetic powder (since the magnetic properties of the final composite material will improve with higher volume loading), the micromachining-compatible processes used to make the finished magnet, and the required physical and chemical properties of the composite (e.g., maximum processing temperature, chemical and thermal resistance, etc.). In this work, polyimide was used as the binder material due to its common use in microelectronics and micromachining, well-known process characteristics, and desirable mechanical and thermal properties. The applicability of polyimide in microelectronics applications has been previously demonstrated [7], [8].

Magnetically hard powders considered in this work fall into two broad categories: ceramic ferrites (e.g., barium or strontium ferrites) and rare-earth alloys (samarium-cobalt or neodymium-iron-boron). The environmental stability and chemical reactivities of these magnetic powders are

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TABLE I
COMPARISON OF CANDIDATE MAGNETIC
MATERIALS FOR MAGNETIC COMPOSITES [9]

Materials Class	Rare Earth Alloys	Ceramic Ferrites
Residual Induction B_r	~ 0.9 Tesla	~ 0.36 Tesla
Intrinsic Coercivity H_{ci}	~ 1200 kA/m	> 320 kA/m
Maximum Energy Product $(BH)_{max}$	~ 155,000 T•A/m	~ 25,000 T•A/m
Chemical Stability	Corrosion Sensitive	Very Stable
Powder Form	Not Commonly Utilized	Commonly Utilized
Particle Size	50 μm - 250 μm	1 μm - 1.5 μm
Relative Cost	High	Low

dramatically different as are their magnetic properties, nominal particle size, and relative cost. These parameters are summarized in Table I, which is taken from [9]. In terms of magnetic properties, e.g., intrinsic coercivity H_{ci} , residual magnetic flux density B_r , and maximum energy product $(BH)_{max}$, the rare-earth alloys possess better magnetic characteristics than the ceramic ferrites. However, it is not easy to find the rare-earth alloys in fine-powder form. Instead, large-particle sizes (50–250 μm) are typically available. Moreover, they are susceptible to oxidation and corrosion (especially in fine-powder form), which results in substantial degradation of their magnetic properties. Ceramic ferrites, although possessing lower values of B_r , H_{ci} , and $(BH)_{max}$ do not suffer from oxidation and corrosion. In addition, they are by far the most widely used type of permanent magnet material due to their availability and low cost. For example, strontium ferrites are available with typical values of $B_r = 0.36$ T, H_{ci} over 320 kA/m, and $(BH)_{max} = 25\,000$ T•A/m. These are fine-particle magnets made by powder metallurgical methods. During their production, the powder may be milled to particles that are approximately single domain size (about 1- μm diameter). This fabrication process results in the magnetic properties of these ceramic ferrites being based on magnetic anisotropy, which produces a magnet with a high intrinsic coercivity and an almost square second quadrant $4\pi M$ versus H characteristic. Their great popularity is mainly due though to the low cost and great abundance of their raw materials. Due to the above-described manufacturing method, strontium ferrite can be easily found in powder form with low particle size (1–1.5 μm) and low cost. In addition, these ferrites are very stable chemically. Due to all these reasons, strontium ferrite powder was selected as the filler material in the magnetic composite.

III. COMPOSITE PREPARATION

The magnetic polymer composite is composed of strontium ferrite particles (Hoosier magnetics) of chemical composition $\text{SrFe}_{12}\text{O}_{19}$ [average particle size 1.15–1.5 μm and Dupont PI-2555 polyimide (a benzophenone tetracarboxylic dianhydride-oxydianiline/metaphenylene diamine formulation)]. The polyimide is supplied as a polyamic acid in an *N*-methylpyrrolidone solvent. Before introducing various quantities (loadings) of the magnetic particles into the polyimide matrix, the polyimide is treated by

addition of isopropyl-trisostearyl-titanate (KR-TTS, Kenrich Petrochemicals), which improves the dispersion of the inorganic magnetic powder into the organic matrix [10]. The materials are mixed using a ball mill rotating at 4–5 rpm. The mixing period is held for at least 72 h in order to ensure homogeneity of the composite solution. The polymer/ferrite liquid suspension is then deposited on a suitable substrate and patterned, e.g., by screen printing or spin-casting followed by photolithography. After deposition and patterning, the magnetic composite is cured to achieve its final mechanical properties. After curing, the polymer magnet is exposed to an external magnetic field to compensate the reversible remanence loss due to exposure of the material to the polyimide cure temperature (300 °C). As the Curie temperature of the strontium ferrite is 450 °C, the remanence losses are reversible and can be overcome by remagnetization. In addition, the remagnetization step defines the preferred direction of permanent magnetism in the final polymer magnet.

The polymer magnet composites are prepared by weight, and weight and volume percentages in the final cured composites are determined as described below. The weight of ferrite powder incorporated into each polymer sample is directly measured. The weight of the polyimide in the cured film is calculated using the average percent solids of the as-supplied polyimide solution in combination with the known quantity of polymer solution used in preparing a particular composite. Weight percentages in the final cured film are transformed into volume percentages using the nominal density values for strontium ferrite and polyimide (5.1 and 1.1 g/cm³, respectively). It is found that many of the measured magnetic and mechanical properties correlate more closely with volume percent loading of ferrite in the composite.

IV. MAGNETIC PROPERTIES

Specimens for magnetic tests were square magnetic polymer sheets deposited on square glass slides by using a multicoat procedure. Standard polyimide processing techniques were adapted for composite deposition and cure. A single coat of the multicoat procedure consists of a 3000-rpm 40-s spin cycle of the magnetic polymer liquid suspension followed by a 15-min soft bake at 120 °C. Three coats are used to produce a final film thickness, after PI curing, between 10–20 μm , depending on the ferrite loading concentration. The multicoat is then fully cured at 300 °C for 1 h in a conventional oven. Upon final cure, the films are exposed to an external magnetic field with a value of 800 kA/m. Finally, the polymer magnet films are removed from their glass substrates for testing. The typical test sample size was 6 mm \times 1 mm. The magnetic properties were measured in the plane of the sample.

Magnetic properties were measured by a vibrating sample magnetometer recording the hysteresis curve of the material, or magnetic moment m (emu) as a function of the applied magnetic field H (A/m). The dependence of the magnetization $4\pi M(T) = 4\pi m/V$, where V is the volume of the studied sample, as a function of the applied magnetic field can then be deduced. From this dependence, the intrinsic coercivity H_{ci} (A/m) and the residual magnetic flux density B_r (T) can

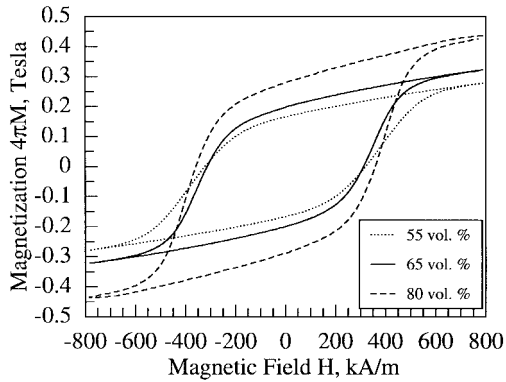


Fig. 1. Magnetization curve $4\pi M$ versus H for three samples with different magnetic powder loading concentrations: 55%, 65%, and 80% by volume.

be determined. Then, the B - H curve, i.e., the curve of the magnetic induction B (Gauss) = $4\pi M + H$ as a function of the applied magnetic field H can also be deduced. The external energy product (an overall measurement of the strength of the magnet) can be obtained by plotting the product of the value of B and H for every point on the demagnetization curve (or second quadrant of the B - H curve) as a function of B . The energy available is zero at both H_c (since $B = 0$ at H_c) and B_r (since $H = 0$ at B_r) points and reaches a peak at a point known as the maximum energy product $(BH)_{\max}$.

Fig. 1 shows the magnetization curves of three samples with different loading of ferrite powder: 55%, 65%, and 80% by volume. From these curves, H_{ci} and B_r were determined. For an 80% by-volume loaded sample, an intrinsic coercivity H_{ci} around 320 kA/m and residual induction B_r of almost 0.3 T, were achieved. The overall magnetization curve also demonstrates the typical square loop behavior of a permanent magnet. As shown in Fig. 1, B_r increases significantly with increasing concentration of magnetic powder, whereas H_{ci} remains approximately constant for the three different ferrite loadings.

Fig. 2 shows the curve of the external energy product (BH) as a function of B . The maximum energy product $(BH)_{\max}$ is the peak of this curve. Curves for three different loadings (55%, 65%, and 80% by volume) are shown. For the 80% by-volume sample, a $(BH)_{\max}$ of 11900 T · A/m (T · Ampere/m) has been achieved. It appears that the maximum energy product increases with increasing magnetic powder concentration loading. All the magnetic results are summarized in Table II.

V. MECHANICAL PROPERTIES

The mechanical properties of the material are determined by an analysis of the load/deflection behavior of a micromachined laterally loaded flexible membrane [11] of the magnetic polymer material. The load/deflection testing is performed using square membranes of the thin films, which are fabricated on a silicon substrate. The suspended membranes are realized using standard micromachining techniques. In the fabrication process, 2-in ⟨100⟩ wafers are heavily boron doped ($>10^{20}/\text{cm}^3$) to form a p^+ etch-stop layer approximately 3–5 μm thick. A 5000-Å-thick layer of silicon nitride is deposited

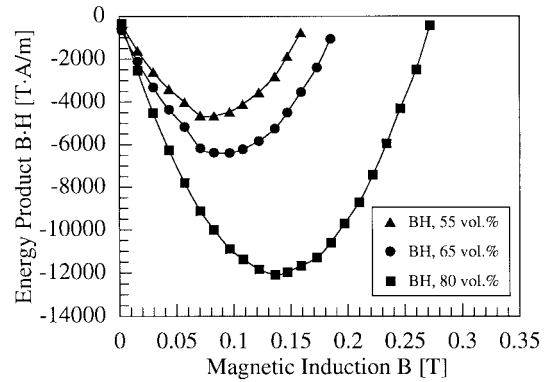


Fig. 2. External energy product curve of three samples with different magnetic powder loading concentrations: 55%, 65%, and 80% by volume.

TABLE II
MAGNETIC PROPERTIES OF POLYMER MAGNETS BASED ON
 $\text{SrFe}_{12}\text{O}_{19}$ OF DIFFERENT VOLUME PERCENTAGE LOADING

Ferrite loading concentration Vol. %	55	65	80	Bulk Ferrite
B_r , Tesla	0.16	0.2	0.28	0.36
H_{ci} , kA/m	~ 320	~ 320	~ 320	> 320
$(BH)_{\max}$, T·A/m	4,780	6,370	11,900	25,000

using plasma chemical vapor deposition (CVD) and is used as an etch mask for both sides of the wafer. Square windows are patterned in the nitride on the unpolished side of the wafer, and the wafer is anisotropically etched from the unpolished side in a 20-weight-percent potassium hydroxide solution at 56 °C to produce a silicon membrane. After the silicon etch is complete, a thin film of magnetic composite material is applied on the polished side of the wafer using the same procedure as for the preparation of magnetic measurement samples. When the composite film has been fully cured at 300 °C for 1 h, the p^+ etch-stop and Si_3N_4 layers are removed from the membrane regions using wet etching, resulting in the finished composite membrane. At this point, the mechanical properties (biaxial modulus and residual stress) can be determined from the load/deflection behavior of the membrane.

The mechanical characteristics are determined by an analysis of the load/deflection behavior of a membrane using an energy minimization approach [12], but modified to account for the presence of residual tensile stress and square dimensions [13], [14]. For a membrane of side length $2a$ and thickness t , it can be shown that the relationship between the applied pressure and the deflection at the center of the membrane is given by

$$\frac{Pa^2}{dt} = 3.04\sigma_o + 1.33K\left(\frac{d}{a}\right)^2 \quad (1)$$

where P is the applied pressure, d is the deflection of the membrane, σ_o is the residual stress in the film, and K is the biaxial modulus of the composite film given by

$$K = \frac{E}{1 - \nu} \quad (2)$$

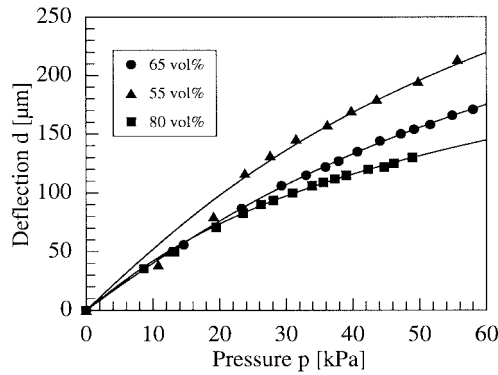


Fig. 3. Typical load/deflection characteristics for the magnetic polymer composites (55%, 65%, and 80% by volume).

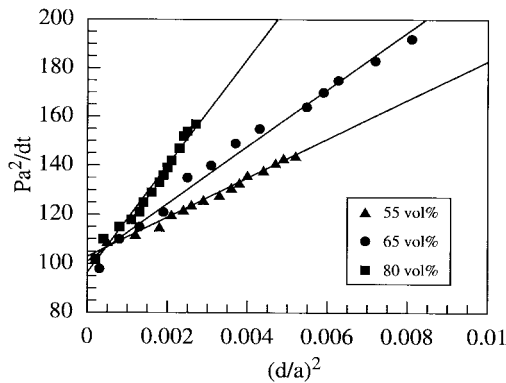


Fig. 4. Load/deflection data plotted in accordance with (1) for the magnetic polymer composites (55%, 65%, and 80% by volume).

where E and ν are the Young's modulus and Poisson's ratio of the film, respectively.

The characterization of the thin films is carried out using a material characterization station, which allows application and simultaneous measurement of a pressure or vacuum load to the membrane. The apparatus is placed on a microscope stage. The deflection of the membrane at its center is measured by focusing on the membrane center and measuring the amount of microscope head travel necessary to keep the membrane in focus using a z -axis Digimatic indicator mounted on the microscope head. Fig. 3 shows typical load-deflection data taken in this manner of 55%, 65%, and 80% by-volume composite membranes. Examination of (1) shows that if pressure-deflection data are plotted with Pa^2/dt on the y axis and $(d/a)^2$ on the x axis, the data should fall on a straight line. The residual stress can then be determined from the y intercept of the line and the plane strain modulus from the slope of the line. Fig. 4 shows the load-deflection data plotted in accordance with (1) for a single membrane of each composite (55%, 65%, and 80% by volume). Similar measurements and data analysis were made on several membranes of each composites (55, 65, and 80), which gives the average values of K and σ_0 (see Table III).

VI. PROCESSABILITY OF THE MAGNETIC COMPOSITE

The realized polymer magnetic composite can be patterned in different ways. Screen-printing deposition is an attractive

TABLE III
MECHANICAL PROPERTIES OF POLYMER MAGNETS BASED ON $\text{SrFe}_{12}\text{O}_{19}$ OF DIFFERENT VOLUME PERCENTAGE LOADING

Ferrite Concentration Loading, vol. %	55 vol. %	65 vol. %	80 vol. %
$K = \frac{E}{1-\nu}$, GPa	6.6 ± 0.6	8.4 ± 0.2	16.7 ± 1.1
σ_0 , MPa	33.3 ± 0.3	34.9 ± 0.4	31.9 ± 0.2



Fig. 5. Screen-printed magnetic polymer composite (80% by volume) with 250- μm features.

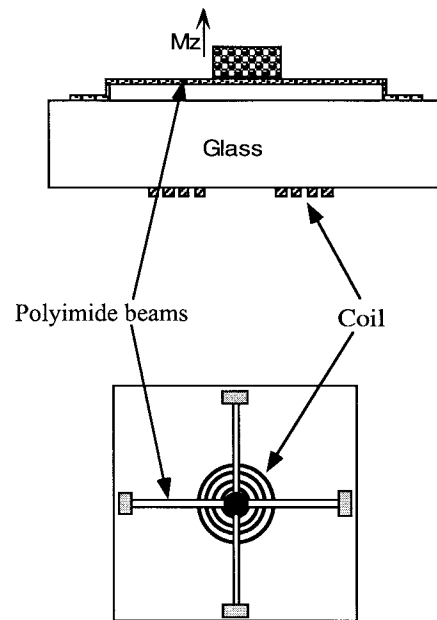


Fig. 6. Schematic view of the fabricated microactuator.

technique due to its capacity to produce thick devices, which are important for force generation in magnetic microactuators (100- μm -thick devices have been produced without difficulty). Using this technique, magnets ranging from 250 μm to centimeters in width can be easily achieved. Fig. 5 shows a screen-printed film with 250- μm features and 100- μm thickness. Moreover, it has also been demonstrated that this material can be patterned by using standard photolithography and wet etching of the polyimide composite. The process is based on alkaline etching of soft-cured polyimide and consists of spin-coat deposition of the magnetic polymer composite followed by a soft bake. Standard positive photoresist is then deposited on the top of the composite, soft baked, and exposed in

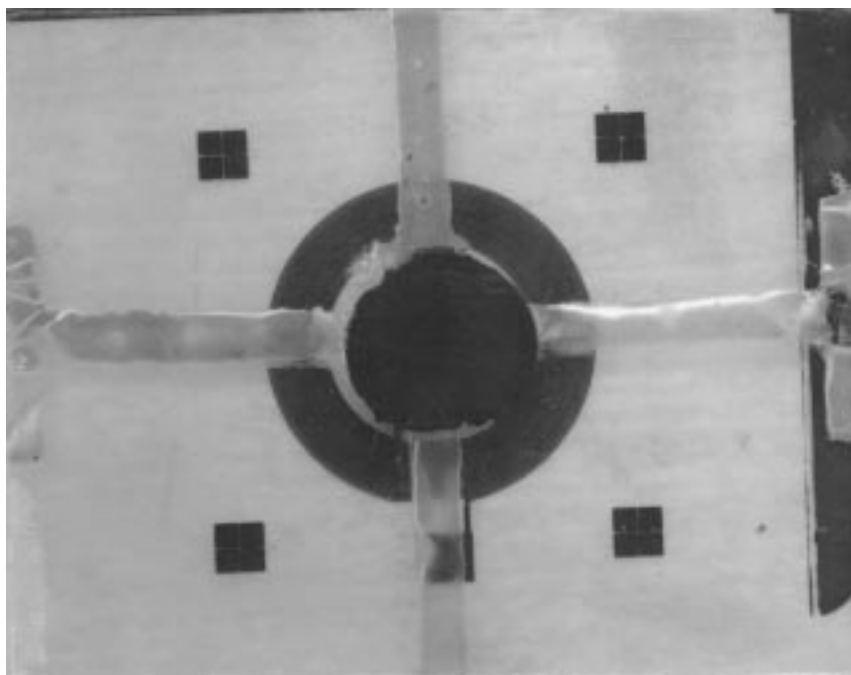


Fig. 7. Photomicrograph of the fabricated microactuator.

the desired pattern. Upon developing in a standard alkaline developer, the exposed regions of the composite, where the photoresist is developed away, are simultaneously etched. After development (and simultaneous etching), followed by residual photoresist removal, the composite is fully cured. Devices on the order of $200\ \mu\text{m}$ in width have been fabricated using this technique.

VII. APPLICATION TO A PROTOTYPE MICROACTUATOR

In order to demonstrate the application of these materials to micromachining, a simple magnetic microactuator incorporating the magnetic composite (Fig. 6) has been fabricated and tested [15]. A 1-mm glass slide is used as the substrate. On the front side of the substrate, a screen-printed circular magnet prepared from the materials described above is supported by a polyimide mechanical flexure. On the back side of the substrate, a circular 21-turn planar coil, with inner and outer diameters of 4.2 and 6.6 mm, respectively, is fabricated using standard photolithography and electroplating techniques. Fig. 7 shows a photograph of a fabricated microactuator. By applying a current to the coil, a magnetic field H (with z -component H_z) is created. Since the center of the magnet is outside the plane of the coil, a magnetic field gradient is created. Thus, an electromagnetic force F_z is created, which is proportional both to the magnetic field gradient and the magnetization of the magnet in the z direction. Fig. 8 shows the deflection of the magnet at its center as a function of current applied to the coil. As expected, a linear relationship between deflection and current is achieved. By reversing the direction of the current, both attraction and repulsion of the actuators could be achieved over a range of approximately $\pm 25\ \mu\text{m}$. The ability of both attract and repel the actuators confirms the permanent magnet character of the material.

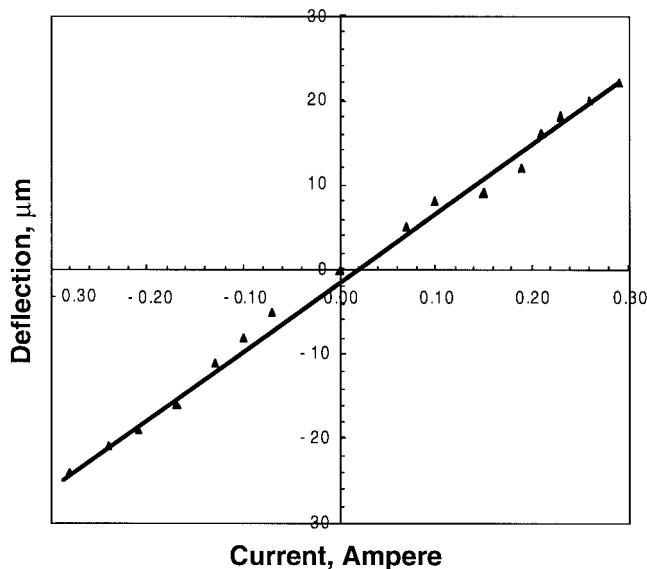


Fig. 8. Plot of microactuator center deflection versus applied coil current.

VIII. CONCLUSIONS

Magnetic polymer composites, which are compatible with microelectronics and micromachining processes, are realized using a polyimide as the organic matrix material and strontium ferrite powder as an embedded inorganic magnetic material. The fabricated composites exhibit good hard magnetic properties: square magnetization curves, and for 80% by-volume samples, a high coercivity H_{ci} around 320 kA/m, a residual induction B_r approaching 0.3 T, and a maximum energy product $(BH)_{\text{max}}$ of 11900 T · (A/m), which compare favorably with bulk ferrite. The mechanical properties of the materials are comparable to the polyimide matrix with residual stresses on the order of unloaded polyimide and

Young's modulus slightly higher than unloaded polyimide (with modulus increasing as loading increases). The composite can be deposited and patterned in a variety of ways, including screen printing or standard photolithography combined with wet etching. The application of these materials to microactuators has been demonstrated through the fabrication of a simple prototype microactuator. Due to its combination of good magnetic properties, mechanical properties, and processability, this material can be useful in a variety of applications, including microactuators, microsensors, integrated inductive components and power conversion devices, and on-chip or on-package electromagnetic shielding applications.

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