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Pulsed Laser Deposition of Nanoporous Cobalt Thin Films

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Abstract

Nanoporous cobalt thin films were deposited on anodized aluminum oxide (AAO) membranes at room temperature using pulsed laser deposition. Scanning electron microscopy demonstrated that the nanoporous cobalt thin films retained the monodisperse pore size and high porosity of the anodized aluminum oxide substrates. Temperature- and field-dependent magnetic data obtained between 10 K and 350 K showed large hysteresis behavior in these materials. The increase of coercivity values was larger for nanoporous cobalt thin films than for multilayered cobalt/alumina thin films. The average diameter of the cobalt nanograins in the nanoporous cobalt thin films was estimated to be ~5 nm for blocking temperatures near room temperature. These results suggest that pulsed laser deposition may be used to fabricate nanoporous magnetic materials with unusual properties for biosensing, drug delivery, data storage, and other technological applications.

Keywords

A. Magnetization curves; B. Epitaxial films; C. Magnetic nano-networks

Introduction

Over the past several years, nanoporous membranes have attracted significant interest due to their potential use in high density data storage, biosensing, drug delivery, and other technological applications.[1–3] Masuda et al. demonstrated that anodization of aluminum, stripping of the thick aluminum oxide layer, and re-anodization of aluminum may be used to produce anodized aluminum oxide (AAO) membranes that exhibit monodisperse pore size and high porosity.[4] Anodized aluminum oxide membranes have recently been used as templates for developing nanowires, nanotubes, and several other nanostructured materials.[5–8] For example, magnetic nanoparticles and nanowires were previously been fabricated within the nanosize pores of anodized aluminum oxide membranes using electrochemical methods. The use of anodized aluminum oxide membranes as templates for growth of magnetic nanoparticles and nanowires obtained has previously been reported.[5, 6, 9–10]

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The development of magnetic metal nanostructures using nanoporous membranes is an emerging area of nanotechnology research. Many interesting magnetic nanostructures have been developed using nanoporous templates, including magnetic antidots and magnetic networks.[11–13] Unlike magnetic nanodot structures (e.g., magnetic nanodots dispersed in nonmagnetic matrix), magnetic antidot structures include nonmagnetic nanoparticles in magnetic media and nanoporous magnetic structures. Magnetic antidots have attracted significant attention due to their potential use as ultra-high-density magnetic storage media. Unlike dot arrays, the stability of written bits increases with storage density in antidot arrays.[14] In addition, antidot arrays or magnetic networks demonstrate no superparamagnetic lower limit to bit size. Common methods for developing magnetic antidot arrays include electron beam lithography and ion beam milling.[14–16] Magnetic antidot arrays also may be prepared by replicating the surface structure of a porous material with a thin layer of a magnetic material. Magnetic antidots have previously been reported by depositing thin films of nickel, cobalt, and cobalt-iron on anodized aluminum oxide membranes using RF magnetron sputtering[17] and DC magnetron sputtering.[14]

In this work, we report on growth of nanoporous cobalt thin films deposited on anodized aluminum oxide substrates using a line-of-sight physical vapor deposition process known as pulsed laser deposition. In pulsed laser deposition, an excimer laser is used to ablate the cobalt target. A plasma plume containing excited atoms and ions forms perpendicularly to the target and expands with a velocity of ~10^6 cm/s. The excited species then form a thin film on the anodized aluminum oxide substrate. Pulsed laser deposition is a convenient and efficient method for growing metallic thin films at room temperature, including antidot structures. In this study, the surface morphology and the magnetic properties of the nanoporous cobalt films were systematically investigated. The magnetic properties of nanoporous cobalt films were also compared with those of continuous cobalt thin films using a physical property measurement system in conjunction with a vibrating sample magnetometer attachment. These nanoporous magnetic materials have numerous potential applications, including use in biosensing, drug delivery, data storage, and other technological applications.

Experimental details

An ultra high purity cobalt target and an ultra high alumina target were supplied by a commercial source (Alfa Aesar, Ward Hill, MA, USA). Anodized aluminum oxide membranes with average pore diameter values of ~200 nm were also obtained from a commercial source (Whatman, Brentford, England). The membranes have thickness values of ~60 μm and porosity values between 25%−50%. 2 cm^2 pieces of 2.5 ohm/cm^2 (p-type), 525 μm thick silicon (100) wafers (Silicon Quest International, Santa Clara, CA) were cleaned with acetone and methanol in an ultrasonic cleaner. The silicon wafers were dipped in hydrofluoric acid to remove silicon oxide and produce a hydrogen-terminated surface. The substrates and targets were loaded into a pulsed laser deposition chamber, which was evacuated to a pressure of 5×10^{-7} Torr.

A Compex 205 KrF (λ = 248 nm) excimer laser (Coherent, Fort Lauderdale, FL) was used for ablation of cobalt and alumina targets. The laser was operated at a frequency of 10 Hz, a pulse duration of 25 ns, and a laser energy density of ~3 J/cm^2. The target-substrate distance was maintained at 4.5 cm, and the target was rotated at a rate of 5 revolutions per minute during the deposition process. Nanoporous cobalt thin films were grown on nanoporous alumina membranes using deposition times of one minute or two minutes. Continuous cobalt thin films were deposited on silicon wafers using deposition times of one minute or two minutes. In addition, multilayered cobalt/alumina films were deposited on silicon wafers.

The multilayered cobalt/alumina films were obtained by alternately ablating a cobalt target with 100 laser pulses and a alumina target with 150 laser pulses a total of four times.

High resolution transmission electron microscopy (HRTEM) was performed using a 2010 analytical electron microscope (JEOL, Tokyo, Japan). Surface morphology of the films was determined using a 6400F field emission scanning electron microscope (JEOL, Tokyo, Japan). Temperature and field dependence of magnetization were measured using a physical property measurement system in conjunction with a vibrating sample magnetometer attachment (Quantum Design, San Diego, CA, USA). The magnetic fields were swept between −20 to +20 kOe. Measurements were obtained at temperatures between 10 and 350 K.

Results and discussion

Figure 1 shows the cross-sectional transmission electron micrograph of a cobalt/alumina multilayered structure. The micrograph demonstrates that a multilayered film containing four alternating cobalt/alumina layers was obtained. The average thickness of the cobalt layers within the multilayered film was estimated as ~1 nm and the average thickness of the alumina layers within the multilayered film was estimated as ~3 nm. These results suggest that the cobalt deposition rate for the deposition parameters used in this study was ~0.1 Å/pulse.

Figure 2 (a) and (b) demonstrate the surface morphology of nanoporous cobalt thin films grown on anodized aluminum oxide membranes for one minute and two minutes, respectively. Using the estimated cobalt deposition rate of 0.1 Å/pulse, the thickness of the cobalt thin films grown for one minute and two minutes was projected as ~6 nm and ~12 nm, respectively. The relatively monodisperse pore size and high porosity of the nanoporous alumina substrate was maintained in the cobalt thin film. In a recent study, the authors have demonstrated nanoporous alumina membranes coated using pulsed laser deposition exhibited slightly larger pore sizes than the as-prepared membranes.[18] An increase in pore size resulted from localized heating of the nanoporous alumina membrane during the film deposition process. In the previous study, the coated nanoporous alumina membranes exhibited hardness and Young’s modulus values slightly lower than those of as-prepared nanoporous alumina membranes due to their slightly larger pore sizes.

Figure 3 shows the hysteresis loops for nanoporous cobalt thin films grown on anodized aluminum oxide membranes for one minute or two minutes. Measurements were obtained with the magnetic field applied parallel to the sample surface. Magnetization of the nanoporous cobalt thin films began to saturate at ~1000 Oe. Large hysteresis loops were observed, which are similar to those commonly observed in ferromagnetic materials. The variation in the coercivity values with respect to temperature is plotted in Figure 4. Both the nanoporous cobalt thin film grown for one minute and the nanoporous cobalt thin film grown for two minutes exhibited coercivity values larger than 1000 Oe at 10 K; the nanoporous cobalt thin film grown for one minute demonstrated larger coercivity value (1120 Oe). At 350 K, the coercivity values decreased to 363 Oe for the nanoporous cobalt thin film grown for one minute and 502 Oe for the nanoporous cobalt thin film grown for two minutes.

The isothermal field dependent magnetization data for the nanoporous cobalt thin film grown on anodized aluminum oxide (deposition time=one minute), the continuous cobalt thin film grown on silicon (deposition time=one minute), and the cobalt/alumina multilayered film are shown in Figure 5. The measurements were obtained at a temperature of 300 K, and the magnetic field was swept between +20000 to −20000 Oe. Compared to the continuous cobalt thin film grown on silicon and the cobalt/alumina multilayered film, the nanoporous cobalt thin film exhibited much larger coercivity values. Coercivity values for the nanoporous cobalt thin film grown for one minute and the nanoporous cobalt thin film grown for two minutes were 385 Oe and 523 Oe, respectively. The values for the nanoporous cobalt thin films are one order of magnitude higher than those for the continuous cobalt thin film grown on silicon (20 Oe) and the cobalt/alumina multilayered film (30 Oe). The relatively high coercivity values were attributed to magnetocrystalline anisotropy and pinning of pores. Figure 6 contains plots of magnetization as a function of temperature for nanoporous cobalt thin film (deposition time=two minutes) measured at 1000 Oe and 2000 Oe. The broad peaks in the magnetization data are attributed to the nanoporous nature of the material and the presence of a blocking temperature near room temperature. The peak in the zero field cooled magnetization results from competition between the larger-sized (relaxed) particles, which contribute to an increase in the magnetic moment, and the superparamagnetic particles, which contribute to a decrease in the magnetic moment of the nanograins inside the nanoporous cobalt thin films. The average size of the grains in the nanoporous cobalt thin film may be estimated from the temperature-dependent magnetization data. The blocking temperature (T_B) for the grains in the nanoporous cobalt thin film approximately varies as $T_B = KV/25k_B$, in which K is the anisotropy constant of metallic cobalt (~ 45×10^5 erg/cm^{-3}), V is the average volume (V) of the pores or the nanoparticles, and k_B is the Boltzmann constant. The average size of the grains in the nanoporous cobalt thin film is ~ 5 nm for a blocking temperature (T_B) of ~300K (Figure 6 inset).

When magnetic field was aligned parallel to the sample surface, the nanoporous cobalt thin films demonstrated high coercivity values. Similar orientation effects have been observed in iron and other magnetic materials.[16] On the other hand, the enhancement of coercivity was not observed when the applied field was aligned perpendicular to the sample surface (Figure 7). Cobalt nanowires exhibit similar magnetic behavior; for example, Li et al. have recently shown that larger coercivity values were observed in magnetic nanowires when the applied field was oriented parallel to the wire axis.[19] The results of this study suggest that shape anisotropy in the nanoporous cobalt thin film may contribute to the enhancement of coercivity.

Conclusions

Nanoporous cobalt thin films were fabricated on nanoporous alumina membranes using pulsed laser deposition performed at room temperature. The nanoporous cobalt thin films retained the monodisperse pore size and the high porosity of the anodized aluminum oxide substrates. The coercivity of nanoporous cobalt thin films was much higher than that of continuous cobalt thin films. The average size of the nanograins in nanoporous cobalt thin films was estimated to be ~5 nm for blocking temperatures occurring near room temperature. Pulsed laser deposition may be used to fabricate nanostructured materials with unusual magnetic properties for biosensing, drug delivery, data storage, and other technological applications.

Acknowledgments

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Biographies

Ravi Aggarwal received a B.S. degree in Chemistry from the University of Delhi and an M.S. degree in Metallurgy from the Indian Institute of Science, Bangalore. Mr. Aggarwal served as a lecturer in the Department of Metallurgical Engineering at the Institute of Technology, Banaras Hindu University (IT-BHU) between 2002 and 2006. He is currently a researcher in Prof. Narayan’s biomaterials group in the Department of Biomedical Engineering at the University of North Carolina.

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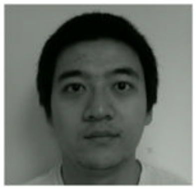
Roger Narayan received his Bachelor's degree in Chemistry, Summa Cum Laude, from North Carolina State University in 1996. He went on to pursue a study of biomaterials at Wake Forest University and North Carolina State University. He currently serves as Associate Professor in the Joint Department of Biomedical Engineering at the University of North Carolina.

Dr. Sudhakar Nori received a Master's degree in Physics from Indian Institute of Technology Roorkee and a Ph.D. degree in Physics from Indian Institute of Technology Kanpur, India. His doctoral dissertation was on electron transport and magnetization studies of layered manganites. He joined NSF Center for Advanced Materials and Smart Structures, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC as a Research Associate in January 2006. He has performed research on several classes of oxide materials, including high temperature superconductors, carbon-based fullerenes, colossal magnetoresistive materials, diluted magnetic semiconductors, as well as cobalt-based nanostructures. He has approximately forty peer-refereed journal publications and conference proceedings.



Wei Wei received a B.S. degree in Physics from the University of Science and Technology of China. He is currently a Ph.D. student in Prof. Narayan's biomaterials group in the Department of Biomedical Engineering at the University of North Carolina.

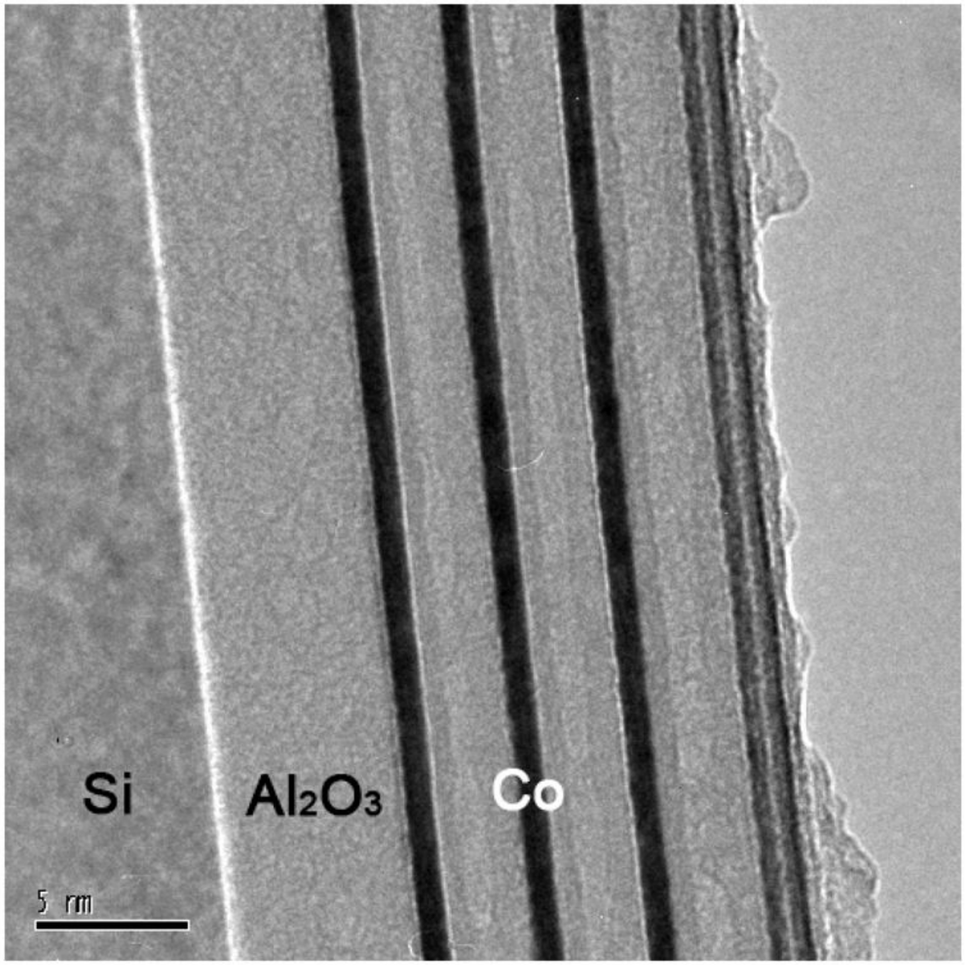


Figure 1.

Transmission electron micrograph of cobalt/alumina multilayered film. The thickness of cobalt layers in the multilayered film is ~1 nm.

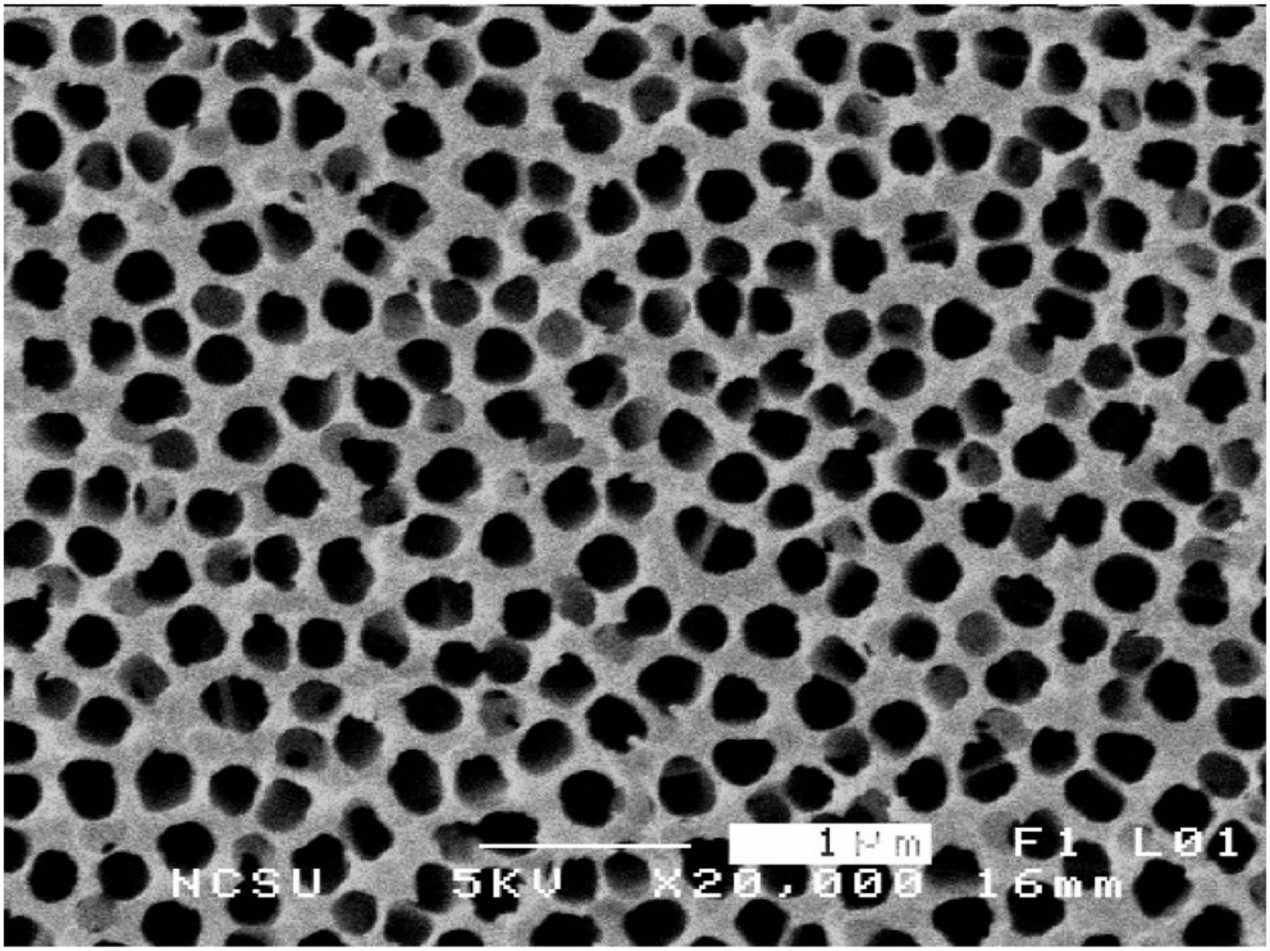


Figure 2 (a)

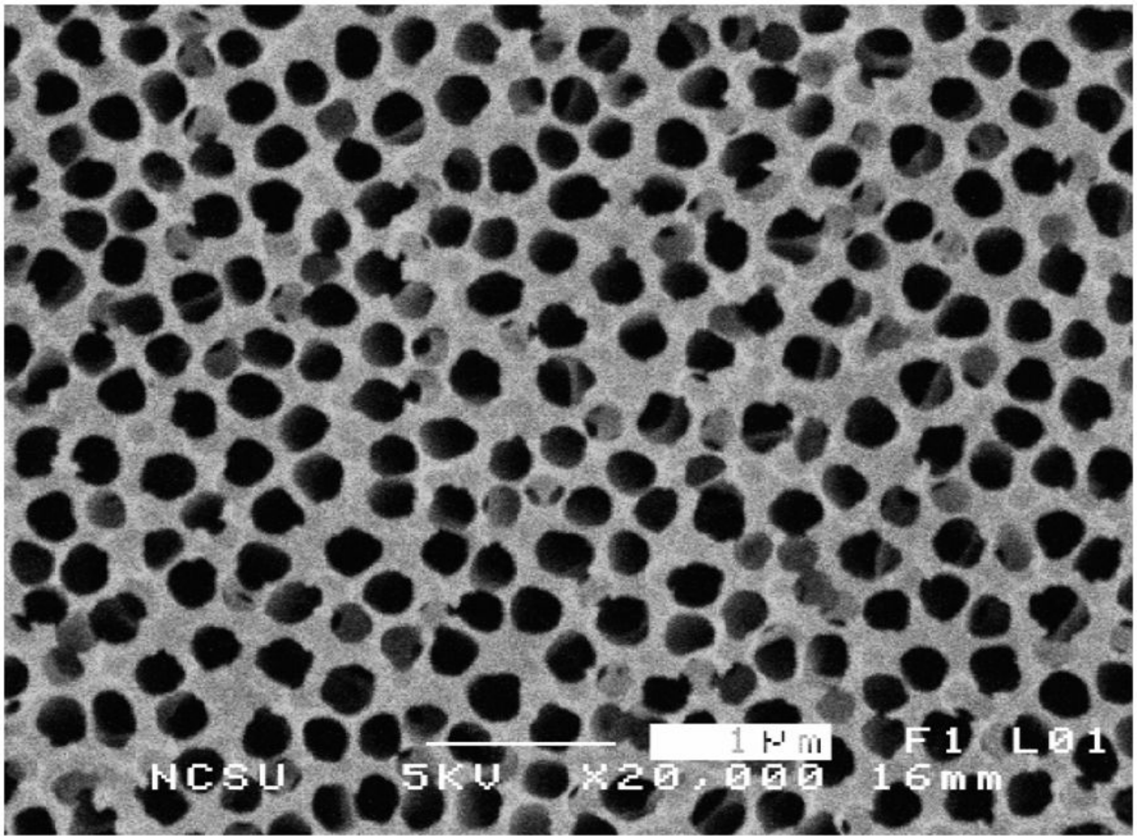


Figure 2 (b)

Figure 2.

Scanning electron micrographs of nanoporous cobalt thin films grown on anodized aluminum oxide membranes (a) Nanoporous cobalt thin film grown for one minute (film thickness ~ 6 nm). (b) Nanoporous cobalt thin film grown for two minutes (film thickness ~ 12 nm).

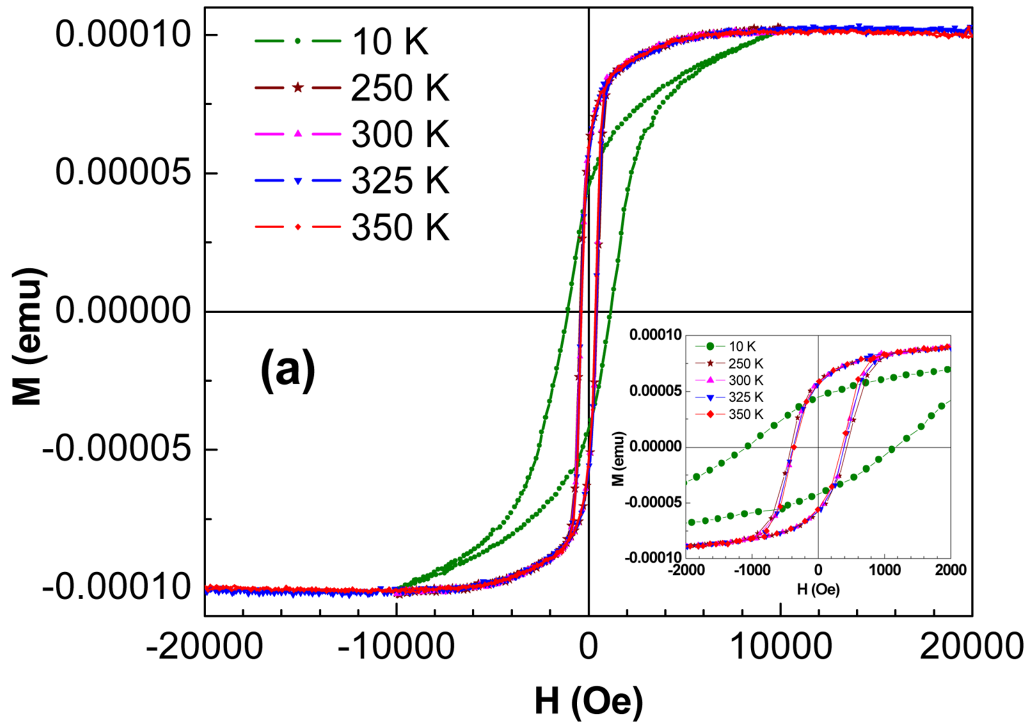


Figure 3 (a)

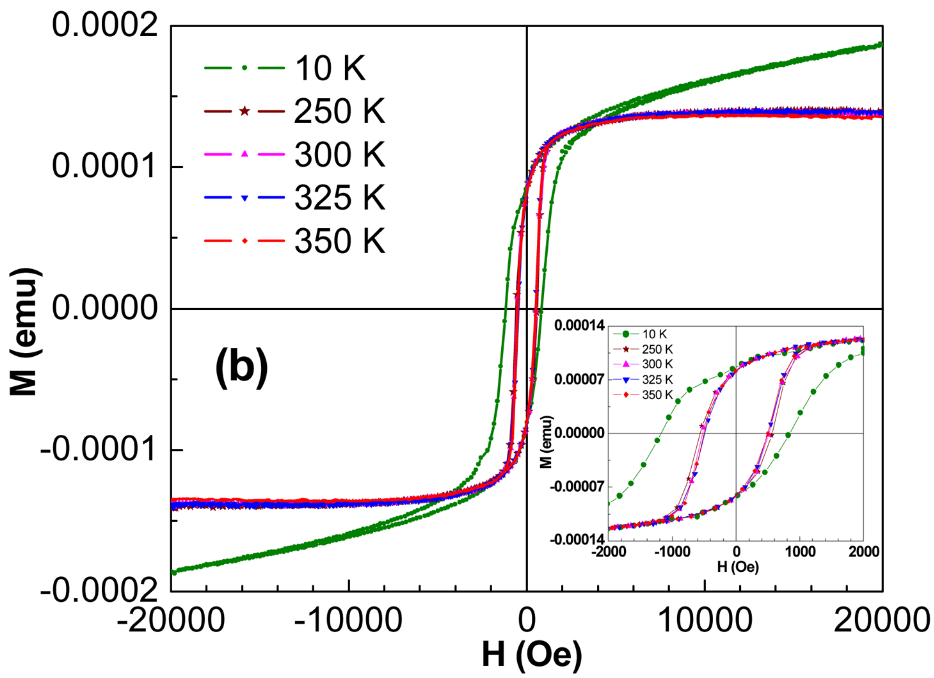


Figure 3 (b)

Figure 3.

Isothermal field dependent magnetization for nanoporous cobalt thin films grown for one minute and two minutes on anodized aluminum oxide membranes. Measurements were obtained at 10, 250, 300, 325 and 350 K. The inset plots of (a) and (b) clearly show the large hysteresis exhibited by these materials. The coercivity values obtained at 10 K (1080 Oe for the nanoporous cobalt thin film grown for one minute and 1160 Oe for the nanoporous cobalt thin film grown for two minutes) were much larger than the values obtained at higher temperatures.

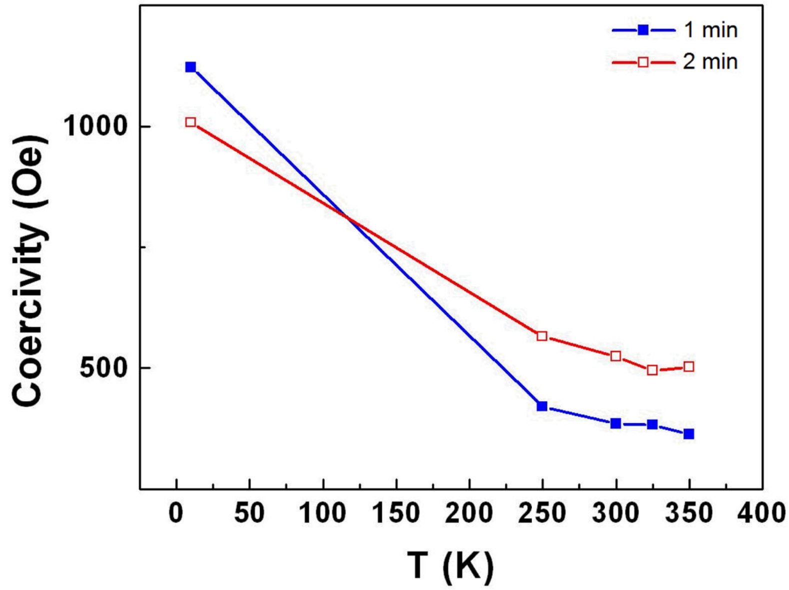


Figure 4.
Coercivity vs. temperature for nanoporous cobalt thin films grown for one minute and two minutes on anodized aluminum oxide membranes.

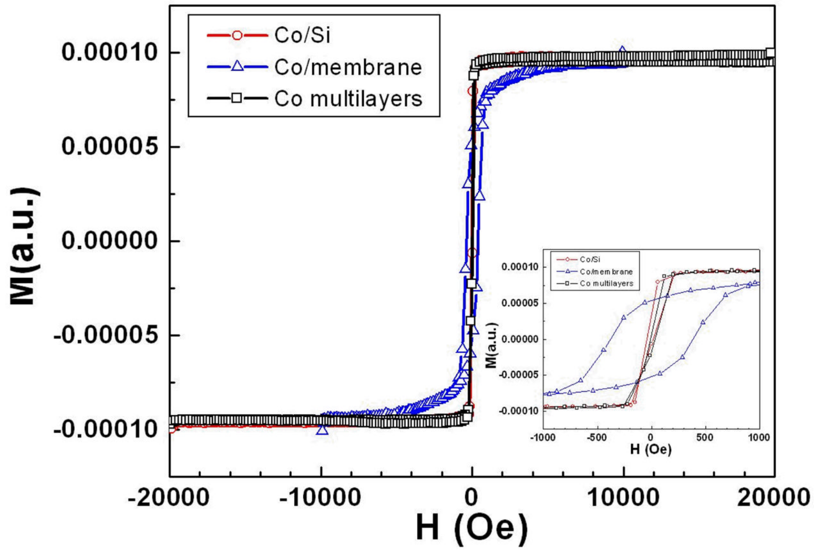


Figure 5.

Isothermal field dependent magnetization of nanoporous cobalt thin film (deposition time=one minute), continuous cobalt thin film (deposition time=one minute)), and cobalt/alumina multilayered film obtained at 300 K.

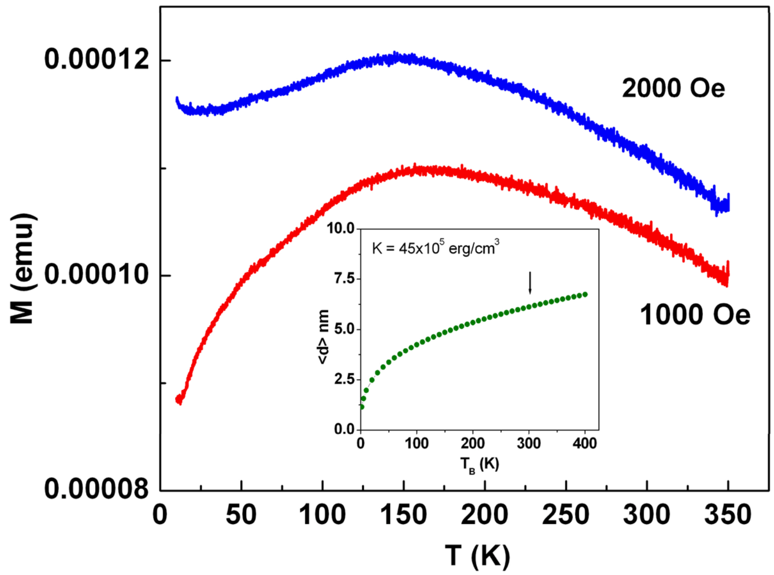


Figure 6.
Magnetization as a function of temperature for nanoporous cobalt thin film (deposition time=two minutes) measured at two different field strengths. The inset shows variation of the average size of the cobalt nanograins with blocking temperature.

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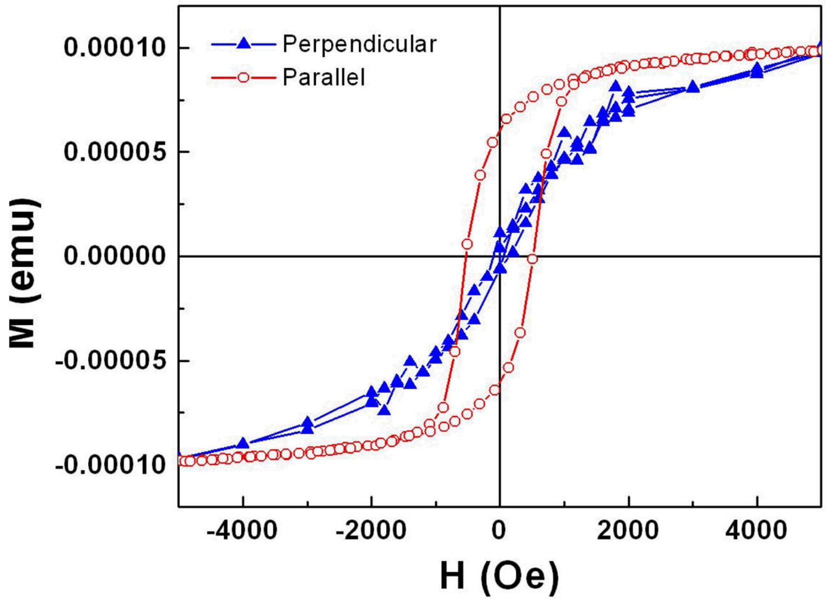

Figure 7.
Isothermal field dependent magnetization of nanoporous cobalt thin film (deposition time=two minutes) obtained with applied magnetic field aligned in both perpendicular and parallel directions with respect to the sample surface at 300 K.