View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by The University of Akron

The University of Akron
IdeaExchange@UAkron

Chemical and Biomolecular Engineering Faculty Research

Chemical and Biomolecular Engineering Department

7-1-2006

High-voltage Parallel Writing on Iron Nitride Thin Films

N. Farkas

J. D. Ehrman

Edward A. Evans
University of Akron Main Campus, evanse@uakron.edu

R. D. Ramsier

J. A. Dagata

Please take a moment to share how this work helps you through this survey. Your feedback will be important as we plan further development of our repository.

Follow this and additional works at: http://ideaexchange.uakron.edu/chemengin_ideas

Part of the Chemistry Commons

Recommended Citation

Farkas, N.; Ehrman, J. D.; Evans, Edward A.; Ramsier, R. D.; and Dagata, J. A., "High-voltage Parallel Writing on Iron Nitride Thin Films" (2006). *Chemical and Biomolecular Engineering Faculty Research*. 14.
http://ideaexchange.uakron.edu/chemengin_ideas/14

This Article is brought to you for free and open access by Chemical and Biomolecular Engineering Department at IdeaExchange@UAkron, the institutional repository of The University of Akron in Akron, Ohio, USA. It has been accepted for inclusion in Chemical and Biomolecular Engineering Faculty Research by an authorized administrator of IdeaExchange@UAkron. For more information, please contact mjon@uakron.edu, uapress@uakron.edu.

High-voltage parallel writing on iron nitride thin films

N. Farkas
Department of Physics, The University of Akron, Akron, Ohio 44325 and Department of Chemistry, The University of Akron, Akron, Ohio 44325

J. D. Ehrman
Department of Physics, The University of Akron, Akron, Ohio 44325

E. A. Evans
Department of Chemical Engineering, The University of Akron, Akron, Ohio 44325

R. D. Ramsier[a)]
Department of Physics, The University of Akron, Akron, Ohio 44325 and Department of Chemistry, The University of Akron, Akron, Ohio 44325

J. A. Dagata
Precision Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8212

(Received 4 October 2005; accepted 21 November 2005; published 22 June 2006)

We report large area patterning of sputter-deposited FeN thin films by a high-voltage parallel writing technique that was recently developed to modify ZrN surfaces. Systematically patterned 15–100-nm-thick FeN films consisting of features with well-defined sizes and shapes are obtained by applying high dc voltages between a stamp and the samples. During the process the oxide dissolves, exposing the substrate beneath. This controlled breakdown eliminates the need for any postexposure etching. The single-step imprinting method presented here provides an emerging route to fabricate isolated FeN geometrical structures on silicon substrates for magnetic applications. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2167074]

I. INTRODUCTION

There is an increasing demand for structured magnetic materials for magnetoelectronics,[1,2] magnetic data storage and recording,[3–5] and biomagnetic[6,7] applications where the ability to control the areal density, separation, and size of the individual features is essential. Scanning probe microscopy (SPM)-based lithographic techniques have been successfully used to fabricate magnetic nanostructures and devices.[8–11] To obtain arrays of magnetic structures, the existing methods often require multiple processing steps and special instrumentation, making the fabrication time consuming and costly. The ultimate motivation for the work presented here is to develop an alternative benchtop technique to fabricate large arrays of discrete magnetic structures with different geometrical shapes for magnetic resonance imaging (MRI) applications. Our recent study,[12] which demonstrates that enhanced single-tip oxidation on ZrN thin films can be successfully extended to parallel writing,[13,14] provides a starting point to create arrays of well-defined features on FeN thin films.

II. EXPERIMENTAL METHODS

Iron thin films were deposited on boron-doped *p*-type Si(111) and Si(100) wafers. Each substrate was ultrasonically cleaned in acetone and isopropyl alcohol (IPA) for 10 min sequentially. Radio-frequency magnetron sputtering was performed at a power of 125 W with a constant argon flow rate of 5 SCCM (standard cubic centimeter per minute). Nitrogen with a flow rate of 5 SCCM was introduced into the sputtering plasma to prepare FeN thin films. The substrate holder, positioned 8 cm above the sputtering source, was grounded and there was no temperature control during deposition. The purity of the Fe target was 99.98% (SCI Engineered Materials). Prior to deposition, the vacuum system was pumped down to 6×10^{-4} Pa using a turbomolecular pump, and the resulting film thickness was measured with a quartz crystal microbalance.

SPM images were taken under ambient conditions at the National Institute for Standards and Technology (NIST) with a TopoMetrix Accurex II operating in contact mode with uncoated silicon cantilevers from Silicon-MDT Ltd. Magnetic force microscope (MFM) imaging was performed using a Digital Instrument NanoScope IV operating in lift mode with Co/Cr-coated silicon tips from Veeco. The compositions of the surfaces of the films were obtained by x-ray photoelectron spectroscopy (XPS). The XPS analyses were performed in fixed analyzer transmission mode under high-vacuum conditions at pressures of $<6\times10^{-6}$ Pa. We used a Kratos ES 300 electron spectrometer with an aluminum anode operated at 12 kV and 10 mA.

III. RESULTS AND DISCUSSION

To extend the high-voltage parallel writing technique to Fe/FeN, silicon master stamps fabricated by standard photolithography at NIST (Ref. 15) are used. The 1×4 cm^2

[a)]Author to whom correspondence should be addressed; electronic mail: rex@uakron.edu

 ©2006 American Vacuum Society

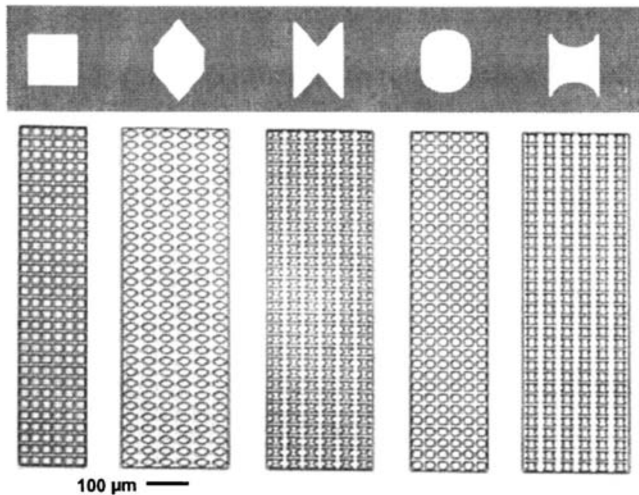

FIG. 1. Optical image of a portion of the silicon stamp consisting of dense arrays of features with synthetic shapes illustrated in the top row. The height of the features is 730 nm.

stamps consist of sparse and dense arrays of 730 nm high features that appear both in positive and negative reliefs, i.e., as posts and wells. Shapes having three different lengths and widths include rectangular features with straight, inward/outward triangular, and inward/outward hemispherical end caps as shown in Fig. 1.

A schematic of the high-voltage parallel writing procedure is depicted in Fig. 2(A). High dc voltages of 200–400 V are applied between the stamp and the substrate for 30 s.

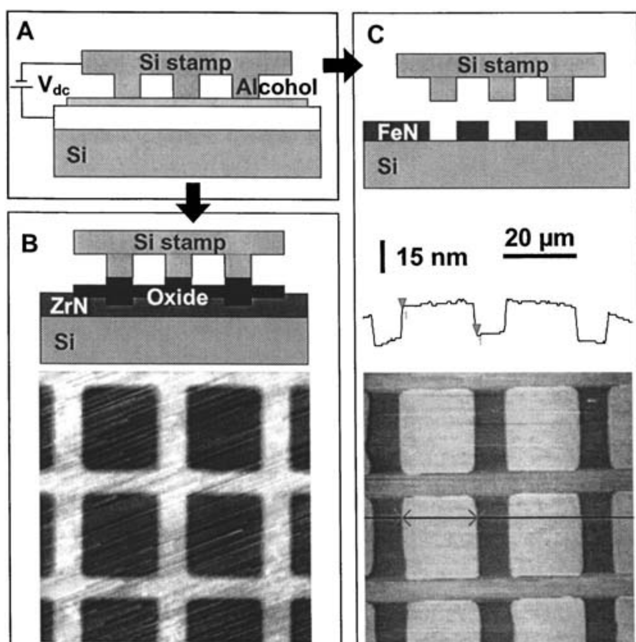

FIG. 2. (A) General representation of the parallel writing technique. (B) Schematic of pattern formation on ZrN and a corresponding SPM image of 70 nm oxide structures (bright). (C) Schematic of pattern formation on a 15-nm-thick FeN film using the same stamp. The oxide dissolves during the process resulting in FeN features (appearing bright in the SPM image) separated by areas of exposed silicon. The film thickness is equal to the feature height obtained from the cross sections.

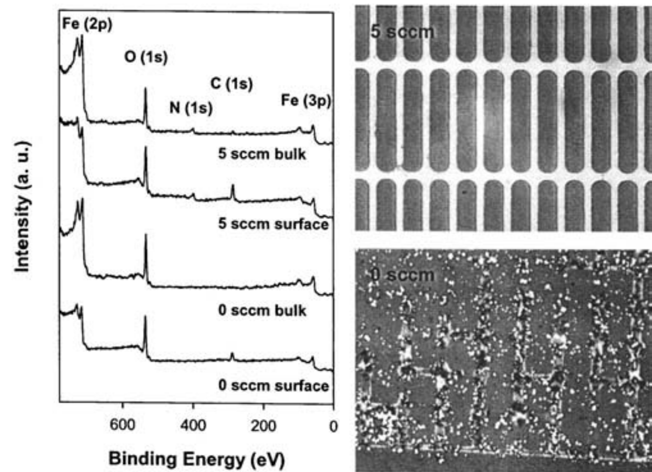

FIG. 3. XPS survey scans of 80-nm-thick iron films sputtered with 0 and 5 SCCM flow rates of nitrogen. Argon sputtering is performed to obtain spectra of the bulk. Optical images of the corresponding patterns formed by applying 300 V for 30 s are shown on the right.

Isopropyl alcohol is used as a compliant medium instead of water,[16] which causes damage to the films during pattern transfer. Many materials can be oxidized under these conditions, but the resulting patterns will differ based on the governing oxidation mechanism. Zr oxidation is driven by oxygen migration,[17] whereas Fe oxidizes by metal ion transport.[18] In our previous study we demonstrated that robust 70-nm high oxide features are generated on ZrN thin films.[12] An example of SPM images of raised oxide features formed on ZrN under the extrusion of the stamp is shown in Fig. 2(B). In the case of FeN presented in Fig. 2(C), the oxide dissolves during the pattern transfer process, revealing the silicon substrate under the raised portion of the stamp.

The formation of holes and dielectric breakdown under extremely high electric fields using single SPM tips has been observed for several materials systems, such as Cr, Al, Fe, and Ti.[19–23] The majority of these metals oxidize by cation diffusion through the growing oxide layer. Dielectric breakdown is often associated with the uncontrolled nature of the single-tip oxidation using very high voltages. Here we demonstrate that high-voltage parallel writing on FeN utilizes the breakdown of the oxide in a controlled and useful way as it eliminates any postexposure etching step.

To verify that the iron oxide formed under the stamp dissolves entirely down to the substrate, FeN films are sputtered on Si(100). As the imprinted films are placed in a 60 °C solution of 83 ml tetra-methyl ammonium hydroxide (TMAH) and 17 ml IPA, the exposed silicon is etched selectively because the FeN pattern serves as an etching mask. In addition, cross-sectional analysis, an example of which is shown in Fig. 2(C) for a 15-nm-thick film, confirms that the heights of the resulting features are equal to the original thicknesses of the FeN films.

To investigate the effect of nitrogen content and thickness of the films, the high-voltage parallel writing process was applied to several Fe and FeN films in a thickness range of 15–200 nm. Figure 3 shows the surface and bulk XPS survey

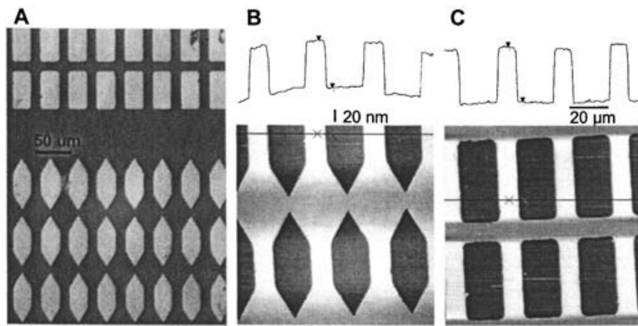

FIG. 4. (A) Optical image of two types of arrays next to each other generated on an 80-nm-thick FeN film. Matching SPM images and cross sections of (B) features with outward triangular and (C) straight end caps are also shown.

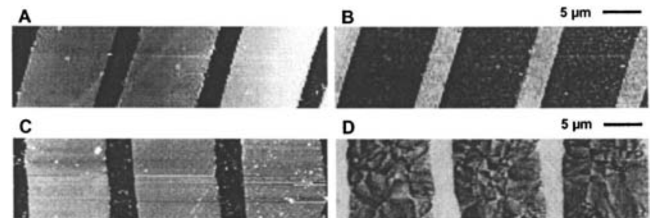

FIG. 5. Simultaneous (A) SPM and (B) MFM images of a patterned 20-nm-thick FeN film deposited by sputtering. Matching (C) SPM and (D) MFM images of a patterned 20-nm-thick iron deposited by evaporation. The exposed silicon substrate appears dark in both SPM images.

scans of 80 nm films sputtered with 0 and 5 SCCM nitrogen flow rates along with the corresponding patterns formed on their surfaces. The XPS spectra verify the existence of nitrogen throughout the FeN film grown with a 5 SCCM nitrogen flow rate. In addition to surface carbon that almost disappears as the samples are argon sputtered, the films contain considerable amounts of oxygen. The presence of oxygen within the films is consistent with the need to replace water with alcohol as a coupling medium between the stamp and substrate. This is because the presence of oxygen in the films enhances the oxidation, requiring less oxygen from an external source.

SPM oxidation kinetic studies report enhanced oxidation for silicon and group-IV metal nitrides.[24–28] Auger microanalyses have been used to verify the nitrogen to oxygen replacement for ZrN which is partially responsible for the enhanced growth as well.[12] Most likely nitrogen reacts with hydrogen and the resulting ammoniac species leave the reaction zone suppressing the space-charge buildup. Similarly, oxidation becomes enhanced and more controllable on nitrided iron films. The optical images on the right of Fig. 3 show partial oxidation and considerable damage to the Fe film, whereas a completely exposed silicon substrate with well-defined features can be observed on the FeN film. Thickness dependence studies performed on FeN thin films reveal that the resulting iron oxides dissolve, leaving the underlying silicon uncovered when the films are up to 100 nm thick. In the case of thicker films the oxidation below the surface does not reach the FeN/Si interface.

Figure 4 displays more optical and SPM images along with cross sections of arrays of rectangular features with straight and outward triangular end caps. This figure emphasizes the well-controlled size and shape of the objects obtained on FeN and that the high-voltage parallel writing technique is inherently simple to extend to different material systems. The lateral dimensions of the features are determined by the stamp, but by changing the thickness of the films, the height and therefore the volume of the objects can be precisely controlled.

To be used for potential MRI applications, the patterned FeN films have to be magnetic in order to locally alter the magnetic field that will result in signal attenuation by shortening the T_2 relaxation time of the surrounding hydrogen nuclei. Figures 5(A) and 5(B) show simultaneous SPM and MFM images of a patterned 20-nm-thick FeN film, respectively. This film was sputter deposited. The contrast in the MFM image is due to the attractive or repulsive interaction between the magnetized tip and the different magnetic domains. The exposed silicon substrate appears dark in the topographic and bright in the MFM images. The magnetic structure of the FeN features is composed of small randomly oriented ferromagnetic grains. Figure 5(C) presents a SPM image of a pattern generated on a 20-nm-thick iron film deposited by evaporation. In good agreement with the findings on sputtered iron films, high-voltage parallel writing on evaporated iron films is less controllable and reproducible than that on FeN. The matching MFM image of Fig. 5(D) demonstrates that the magnetic domain structures of the films depend on the deposition conditions. Consistent with MFM studies on ultrathin iron films,[29] the evaporated iron films exhibit in-plane magnetization indicated by the cross-tie domain walls.

IV. IMPLICATIONS

Iron oxide particles with biocompatible coatings are extensively used as contrast agents in MRI.[30–33] The iron content of the particles affects the susceptibility-induced decrease in the T_2-weighted MRI signal. Not only the size but the shape of the objects also influences the apparent image distortion. Since the size and iron content of particles show large variations, quantitative analysis of the detection sensitivity and resolution in MRI is rather difficult. These problems could be addressed by imaging arrays of iron nitride features with systematically designed shapes and separation. Controlling the volume of the objects would provide a means of studying the relationship between the MRI signal decrease and the iron content.

V. SUMMARY STATEMENTS

We have demonstrated the versatility of the high-voltage parallel writing technique, developed to modify group-IV metal surfaces, by extending it to magnetic thin films. Systematically patterned FeN thin films consisting of different geometrical features with heights up to 100 nm are obtained. Using extremely high electric field conditions, the oxide dis-

solves under the extrusion of the stamp, leaving the silicon substrate exposed between FeN structures. Consequently, there is no need for additional etching which makes the high-voltage parallel writing technique on FeN a single-step method to obtain well-separated structures. TMAH etching experiments verify that the FeN features are isolated from each other. With precisely controlled height and methodically designed lateral size, the FeN arrays are potential candidates for MRI sensitivity and resolution measurements.

ACKNOWLEDGMENTS

One of the authors (I.A.D.) acknowledges support from Jack Martinez and Steve Knight of the NIST Office of Microelectronics Programs. Another author (N.F.) acknowledges support from NIST-MEI. Another author (R.D.R.) acknowledges support from NIH-NIBIB Grant No. EB003397-01.

[1]M. Bal, A. Ursache, M. T. Tuominen, J. T. Goldbach, and T. P. Russell, Appl. Phys. Lett. **81**, 3479 (2002).
[2]W. J. Gallagher, S. S. P. Parkin, Y. Lu, X. P. Bian, A. Marley, K. P. Roche, R. A. Altman, S. A. Rishton, C. Jahnes, T. M. Shaw, and G. Xiao, J. Appl. Phys. **81**, 3741 (1997).
[3]X. M. Yang, A. Eckert, K. Mountfield, H. Gentile, C. Seiler, S. Brankovic, and E. Johns, J. Vac. Sci. Technol. B **21**, 3017 (2003).
[4]S. M. Weekes and F. Y. Ogrin, J. Appl. Phys. **97**, 10J503-1 (2005).
[5]B. D. Terris, D. Weller, L. Folks, J. E. E. Baglin, A. J. Kellock, H. Rothuizen, and P. Vettiger, J. Appl. Phys. **87**, 7004 (2000).
[6]D. K. Wood, K. K. Ni, D. R. Schmidt, and A. N. Cleland, Sens. Actuators, A **120**, 1 (2005).
[7]D. R. Baselt, G. U. Lee, M. Natesan, S. W. Metzger, P. E. Sheehan, and R. J. Colton, Biosens. Bioelectron. **13**, 731 (1998).
[8]G. Gundiah, N. S. John, P. J. Thomas, G. U. Kulkarni, C. N. R. Rao, and S. Heun, Appl. Phys. Lett. **84**, 5341 (2004).
[9]Y. Takemura and J.-I. Shirakashi, Adv. Eng. Mater. **7**, 170 (2005).
[10]L. Fu, X. Liu, Y. Zhang, V. P. Dravid, and C. A. Mirkin, Nano Lett. **3**, 757 (2003).
[11]M. Hirooka, H. Tanaka, R. Li, and T. Kawai, Appl. Phys. Lett. **85**, 1811 (2004).
[12]N. Farkas, J. R. Comer, G. Zhang, E. A. Evans, R. D. Ramsier, S. Wight, and J. A. Dagata, Appl. Phys. Lett. **85**, 5691 (2004).
[13]M. Cavallini, P. Mei, F. Biscarini, and R. Garcia, Appl. Phys. Lett. **83**, 5286 (2003).
[14]A. Yokoo, J. Vac. Sci. Technol. B **21**, 2966 (2003).
[15]J. A. Dagata and J. S. Suehle (unpublished).
[16]M. Tello and R. Garcia, Appl. Phys. Lett. **83**, 2339 (2003).
[17]F. P. Fehlner and N. F. Mott, Oxid. Met. **2**, 59 (1970).
[18]G. W. R. Leibbrandt, G. Hoogers, and F. H. P. M. Habraken, Phys. Rev. Lett. **68**, 1947 (1992).
[19]S. Melinte, B. Nysten, and V. Bayot, Superlattices Microstruct. **24**, 79 (1998).
[20]R. Held, T. Heinzel, P. Studerus, and K. Ensslin, Physica E (Amsterdam) **2**, 748 (1998).
[21]N. Farkas, J. C. Tokash, G. Zhang, E. A. Evans, R. D. Ramsier, and J. A. Dagata, J. Vac. Sci. Technol. A **22**, 1879 (2004).
[22]C. Niu, N. P. Magtoto, and J. A. Kelber, J. Vac. Sci. Technol. A **19**, 1947 (2001).
[23]F. Qin, N. P. Magtoto, M. Garza, and J. A. Kelber, Thin Solid Films **444**, 179 (2003).
[24]F. S.-S. Chien, Y. C. Chou, T. T. Chen, W.-F. Hsieh, T.-S. Chao, and S. Gwo, J. Appl. Phys. **89**, 2465 (2001).
[25]S. Gwo, C.-L. Yeh, P.-F. Chen, Y.-C. Chou, T. T. Chen, T.-S. Chao, S.-F. Hu, and T.-Y. Huang, Appl. Phys. Lett. **74**, 1090 (1999).
[26]S. Gwo, J. Phys. Chem. Solids **62**, 1673 (2001).
[27]N. Farkas, G. Zhang, K. M. Donnelly, E. A. Evans, R. D. Ramsier, and J. A. Dagata, Thin Solid Films **447–448**, 468 (2004).
[28]N. Farkas, G. Zhang, E. A. Evans, R. D. Ramsier, and J. A. Dagata, J. Vac. Sci. Technol. A **21**, 1188 (2003).
[29]M. Dreyer, D. G. Hwang, and R. D. Gomez, J. Appl. Phys. **91**, 8138 (2002).
[30]E. M. Shapiro, S. Skrtic, K. Sharer, J. M. Hill, C. E. Dunbar, and A. P. Koretsky, Proc. Natl. Acad. Sci. U.S.A. **101**, 10901 (2004).
[31]K. A. Hinds, J. M. Hill, E. M. Shapiro, M. O. Laukkanen, A. C. Silva, C. A. Combs, T. R. Varney, R. S. Balaban, A. P. Koretsky, and C. E. Dunbar, Blood **102**, 867 (2003).
[32]Z. Zhang, E. J. van den Bos, P. A. Wielopolski, M. de Jong-Popijus, D. J. Duncker, and G. P. Krestin, MAGMA **17**, 201 (2004).
[33]H. Yoshioka, Y. Itai, Y. Saida, K. Mori, H. Mori, and T. Okumura, Magn. Reson. Imaging **18**, 1079 (2000).

Copyright of Journal of Vacuum Science & Technology: Part A is the property of AVS, The Science & Technology Society and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.