DOE/ER/45529--T2
CONF-9703106--

"GROWTH INDUCED MAGNETIC ANISOTROPY IN CRYSTALLINE AND AMORPHOUS THIN FILMS"

FRANCES HELLMAN

ANNUAL PROGRESS REPORT, YEAR 4
11/1/97 THRU 10/31/98

UNIVERSITY OF CALIFORNIA, SAN DIEGO
9500 GILMAN DRIVE
LA JOLLA, CA 92093

DOE AWARD NO. DE-FG03-95ER45529

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

Progress report year 4 DOE DE-FG03-95ER45529

July 20, 1998

Principal investigator: Frances Hellman, Dept. of Physics , U.C.San Diego

Summary of previous research 11/1/97-10/31/98:

The work in the past 6 months has involved three areas of magnetic thin films: 1) amorphous rare earth-transition metal alloys, 2) epitaxial Co-Pt and Ni-Pt alloy thin films, and 3) collaborative work on heat capacity measurements of magnetic thin films, including nanoparticles and CMR materials.

1) In the amorphous alloys, we made a systematic study of the effects of local anisotropy, macroscopic (perpendicular) anisotropy, and exchange constant on the fundamental (and practical) properties of these magnetic alloys. We have focused in particular on understanding the cause and the effect of the growth-induced perpendicular magnetic anisotropy. This anisotropy we have shown is caused by surface energy minimization during growth of these thin films. *Bulk* energy minimization, by contrast, produces an isotropic structure. Armed with this understanding of the cause of the anisotropy, we are able to use growth and annealing parameters to control it quite precisely. We prepared a wide range of samples of amorphous (Gd, Dy, Tb)-Fe/Ni with varying concentrations of the rare earths and of the Fe/Ni ratio, allowing control of exchange interaction and local anisotropy energies, and under different preparation conditions to control the macroscopic anisotropy. We have shown that for all values of anisotropy, amorphous Tb-Fe behaves like a ferrimagnet, not a spin glass as expected.

Specifically, we found that the magnetic ordering of a-RFe_2 thin films, where R = Gd, Tb, shows a relatively sharp cusp in the specific heat, with evidence of thermodynamic critical fluctuations, at the same temperature as that measured magnetically, independent of the magnitude of the anisotropy. a-$TbFe_2$ is considered a random anisotropy magnet, in the exchange-dominated low D/J_{ex} regime, while a-$GdFe_2$ has negligible anisotropy. Nonetheless, the specific heat of these two alloys appear nearly identical over the entire temperature range measured, except near their T_c. Virtually all available magnetic entropy is evolved below T_c for both materials, quite unlike what is seen in spin glasses. Sputtered and e-beam evaporated a-RFe_2 samples appear qualitatively similar; there are small shifts in T_c which suggest that the evaporated films are locally denser, despite TEM evidence of larger scale density variations in the evaporated samples. Increasing the growth temperature of either sputtered or e-beam evaporated samples causes a slight increase in T_c, a sharpening of the specific heat peak, and a decrease in high field susceptibility χ. We suggest that this correlation can be understood by assuming that increasing the growth temperature increases the local density and the orientational correlation length R_a and improves the sample homogeneity which causes critical behavior to persist closer to T_c. Annealing of any sample also increases T_c and causes the specific heat peak to sharpen, due again to a more homogeneous, denser sample; χ however is unaffected, suggesting that R_a is not significantly changed.

We have also done extensive small angle neutron scattering (SANS) and magnetic force microscopy (MFM) to characterize the temperature dependence of the ferromagnetic correlation length in amorphous $TbFe_2$ below its magnetic ordering temperature. Previous observations had shown a correlation length limited to 50Å at low temperatures. In our study, samples were prepared under a variety of deposition conditions, giving different macroscopic anisotropy constant K_u, but the same composition and local anisotropy. In all cases, the observed correlation length is greater than 300Å, and appears to be limited by dipolar effects as in a conventional ferromagnetic material. This result is consistent with a recent theory of random magnetic anisotropy materials (by R. Fisch) which suggests that in the exchange-dominated limit, the magnetic order is quasi long range.

2) The work on the epitaxial Co-Pt and Ni-Pt alloys was originally undertaken as a comparison study to the amorphous alloys. Crystalline Co-Pt alloys have many striking similarities to the amorphous rare earth-transition metal alloys: perpendicular magnetic anisotropy (as unexpected in a cubic material like Co-Pt which is fcc as it is in an amorphous alloy), magneto-optic activity, and a T_c (for $CoPt_3$) somewhat above room temperature. This anisotropy is again a growth-surface induced effect: increasing the growth temperature enhances the effect, while annealing eliminates it. We have shown that the anisotropy is 100% correlated with the formation of tiny Co (or Ni) and Pt platelets and have suggested that these platelets are the consequence of a surface-induced immiscibility. We have also shown that Ni-Pt exhibits the same phenomena, as do Co-Pt alloys of other compositions. A crucial question which remains: are we truly probing a surface equilibrium phase, or is this a question of kinetic growth effects.

To probe the structure of these materials, we collaborated on an EXAFS study with V. Harris at NRL, on a Co NMR study with Tom Thomson in England, and an extensive TEM study with Karen Kavanagh here at UCSD. The EXAFS study showed the increased Co coordination that we anticipated based on the magnetization measurements. TEM showed the strain fields resulting from the compositional variations in these epitaxial single crystal films. The Co NMR work was not completed as Dr. Thomson changed jobs. We will explore completing this work with Joe Budnick at U. Conn.

We also explored the ternary Co-Pt-Si system, in the low Si limit, to try to reduce the grain size and hence the S/N ratio relevant to MO recording. We found that introduction of even 1-2% Si was sufficient to eliminate the perpendicular anisotropy and to make the grains less than 100Å diameter. This makes the films not useful for MO, but may leave them as a prospect for in-plane recording, a possibility we are currently exploring via MFM and magnetization measurements.

3) We are currently involved in several collaborations to measure specific heat of magnetic thin films, a measurement made possible by our unique microcalorimeters. One in particular is with Ami Berkowitz in the Center for Magnetic Recording Research. We are using the specific heat to study nanoparticles of various AFM and FM particles in backgrounds of insulating or metallic matrices. The goal is to characterize the properties of individual particles in both interacting and non-interacting limits. Magnetization measurements of antiferromagnetic thin films, nanoparticles, and multilayers may be strongly influenced by the presence of uncompensated surface spins. The specific heat, by contrast, shows unambiguously the ordering of the spins in the bulk of the material, providing an invaluable complement to the magnetization measurements. We are the only people in the world capable of measurements of the specific heat of materials such as these, weighing less than 20 μg.

The other existing collaboration is with Prof. Michael Coey to measure the specific heat of single crystals of various manganates (some of which are the colossal magnetoresistance (CMR) materials). We have looked at several compositions of LaCaMnO, and measured the specific heat both through the FM or AFM phase transition and to low temperatures. This work is still in progress.

Summary of Future Research:

Understanding the source of perpendicular anisotropy, and its effects on the magnetic structure of a thin film, is important both for the materials discussed here where anisotropy is crucial to their proposed or current use and for materials where anisotropy is an unwanted feature (for soft magnetic materials). We have hypothesized that the anisotropy in the crystalline alloys (at least) is due to a growth-surface driven compositional separation (Co and Pt platelets), and that is separation is in turn related to an incomplete surface segregation. It is well known that the equilibrium Co-Pt and Ni-Pt surfaces are 100% enriched in Pt (for (100) and (111) surfaces) and depleted for the (110) surface. What is not known is how this affects growth under conditions where equilibrium is not maintained. In particular, the perpendicular anisotropy occurs for growth temperatures between approximately 0.1 and 0.3 of the melting temperature, a regime where surface mobility is high and bulk mobility negligible. In this regime, it is not clear either theoretically or experimentally how or if surface segregation still occurs at the growth surface, during the approximately 1 second before each layer is buried by the incoming atomic flux. We are working with a manufacturer (Surface Interface) to develop a new tool: a real-time-Auger analysis system, which will allow us to characterize the surface composition in real time as we grow the film. This system will work together with our existing RHEED analysis system which gives surface structural information. These measurements will give us a nearly unique capability (there is one other group in Germany working on a similar system) to characterize the surface of a growing film, fundamentally a different problem than analyzing it after when it has a chance to equilibrate.

In addition to this surface analysis work, the work on anisotropy in both amorphous rare earth-transition metal alloys and crystalline Co-Pt and related alloys will be continued with three approaches. First, we have set up a low energy Ar ion source in the UHV deposition system for ion-assisted deposition. This technique will allow us to use low growth temperatures but still achieve appreciable surface mobility during the growth. We believe that if we can grow at low temperatures where bulk mobility is negligible, but achieve high surface mobility due to gentle bombardment with Ar ions, we may be able to significantly enhance the anisotropy. This will be of technological interest, since growing at low temperatures is crucial for industrial use of these M-O materials, but also will provide a powerful probe to test our proposed surface energy minimization theory. Secondly, we are investigating several ways of modifying the growth of the epitaxial $CoPt_3$ in order to determine how limiting or enhancing surface diffusion and therefore the growth surface affects the final structure and in particular the anisotropy: 1) vicinal substrates at various cut angles to limit surface diffusion, 2) nucleation-limited two stage growth, 3) use of surfactants such as a partial pressure of O_2 during growth. Third, we will continue to explore the effect of changing alloy composition, both within the Co-Pt alloy system and with other Co-X and Ni-X alloys (e.g. Co-Ag and Co-Pd).

Finally, we will continue developing collaborations based on our unique microcalorimeters which allow us to perform specific heat measurements on thin films of magnetic materials, as a function of both temperature and magnetic field. Specific heat is a powerful measurement tool, complementary to magnetic measurements and neutron scattering; it is not an exaggeration to say that we can make measurements on thin films which are three orders of magnitude more sensitive than anyone else in the world. We re-designed the devices to allow higher temperature operation and are currently setting up a high temperature system to allow measurements up to 700°C (currently we are limited to 250°C), which will allow measurements of technologically-relevant materials. We have also set up a high field measurement system which is nearly complete (measurements have been made in fields of 8T from 77K to room temperature; the temperature range below 77K is currently being set up).

Federal Support:

Current

Supporting Agency	Project Title	Award Amount	Period Covered	Man-Months CAL/ACAD/SUM	Location
NSF	In situ determination of thermodynamic, magnetic, and transport properties of doped and undoped thin film C_{60}	$85,000/yr	08/01/92-11/31/98	0	UCSD
DoE	Growth induced magnetic anisotropy in amorphous and crystalline thin films	$100,000/yr	11/01/97-10/31/00	0	UCSD
NSF	Development of instru-mentation for micro-calorimetry of biological systems	$86,507/yr	10/01/95-09/30/98	0	UCSD
NSF	Electron Correlations at the Edge of Instability: (collaborative grant)	$130,000/yr	08/01/97-07/31/00	1	UCSD
DoD (AFOSR MURI)	Novel Nanoscale Devices and Engineered Materials (sub-contract with U. Florida)	$33,300	06/14/98-06/13/99	0	UCSD/U.Flo

Pending:

Supporting Agency	Project Title	Award Amount	Period Covered	Man-Months CAL/ACAD/SUM	Location
NSF	IGERT - Materials: Training at the Intersection of Science, Engineering, and Industry	$414,458/yr (grad training grant)	09/01/95-08/31/98	0	UCSD
DoE	High Energy Exchange-Spring Magnets	$537,753 (5 PI's)	10/1/98-9/30/01	1	UCSD (Arizona State and SUNY/SB)
NSF	MRSEC: Center for Research on Magnetic Nano-structures	$11,573,657 (24 participants)	3/1/99 2/28/04	0	UCSD

Publications:
F. Hellman, E. N. Abarra, and A. L. Shapiro, "Thermodynamic Measurements of Magnetic Ordering in Antiferromagnetic Superlattices", to appear in Sept. 1 Phys. Rev. B.

"Extremely Long Ferromagnetic Correlation Length in Amorphous $TbFe_2$", F. Hellman, A. L. Shapiro, E. N. Abarra, R.A. Robinson, M.R. Fitzsimmons, J. J. Rhyne, and J. I. Suzuki, in final preparation, to be submitted to Phys. Rev. B

"Growth-surface-driven clustering and anisotropy in Co-Pt alloy thin films". A.L. Shapiro, P.W. Rooney, M.Q. Tran, D. Weller, K. Rellinghaus, and F. Hellman, in final preparation, to be submitted to Phys. Rev. B

"Destruction of growth-surface-driven anisotropy in CoPt3 films by Si doping", A.L. Shapiro, B.B. Maranville, O. Vajk, K. Ring, K. Kavanagh, E.N. Abarra, F. Hellman, in preparation, to be submitted to Applied Physics Letters

"Magnetic Order of $Co_{0.1}Pt_{0.9}$ in Proximity to $CoPt_3$", A. Shapiro, F. Hellman, and M. R. Fitzsimmons, MRS Spring Conference Proceedings, 1998.

Presentations:
"Randomness and order in amorphous and crystalline magnetic materials"; F. Hellman colloquia at:
Utah State Jan. 28, 1997
UC Irvine. April 25, 1997.
Maria Goeppert-Mayer Memorial Symposium, UCSD March 8, 1997.
"Magnetic Order in Amorphous Rare Earth-Transition Metal Thin Films", F. Hellman invited talk LANSCE User Group meeting, LANL Aug. 7, 1997.
"Destruction of Growth-Surface-Driven Perpendicular Magnetic Anisotropy in $CoPt_3$ Alloy Films by Si Doping", A. L. Shapiro, O. Vajk, B. M. Maranville, and F. Hellman, March 1997 meeting.
"From Spin Glass to Ferromagnet in Amorphous Tb-Fe", A.L. Shapiro, E. N. Abarra, S. K. Watson, F. Hellman, R. A. Robinson, M.R. Fitzsimmons, and J. J. Rhyne, MMM conference Jan. 1998.
"Tunneling and IR Spectroscopy on Giant Magnetoresistive Amorphous Rare Earth-Silicon Alloys", F. Hellman, P. Xiong, B. L. Zink, P. Henning, D. Basov, and R. C. Dynes, MMM conference Jan. 1998.
"Polarized Neutron Reflectometry Studies of Ferromagnetic Proximity Effect-Induced Moments", A.L. Shapiro, B. B. Maranville, F. Hellman, and M.R. Fitzsimmons, LANSCE User Group meeting, LANL Aug. 7, 1997.
"The Effect of Growth Surface Mobility on Thick Ferromagnetic Alloy Films", A.L. Shapiro, B. B. Maranville, O. Vajk, K. Ring, K. Kavanaugh, and F. Hellman, CLC Workshop Sept 9, 1997.
"Is Magnetic Order Possible in a Non-magnetic Material?", A.L. Shapiro, F. Hellman, and M.R. Fitzsimmons, MRS meeting April 1998.

Personnel associated with program:

In addition to the Principal Investigator, there are currently three graduate students (Alex Shapiro, Brian Maranville, and Dongkyun Kim) involved with the research. Alex Shapiro will be completing his PhD in the next year, on the Co-Pt and Ni-Pt systems. Brian Maranville is working with the ion mill and developing the real-time Auger system to characterize the surface composition during growth. His focus will be on understanding the surface properties which lead to anisotropy. Dongkyun Kim's PhD will center on specific heat of the CMR and related materials, in collaboration with Prof. Michael Coey. I have also offered a post-doctoral position to Vasumathi Dharmavan to work on growth of the crystalline anisotropic materials; she will start in Nov.