DOE/ER/45529--T1
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JUL 22 1996
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Progress report year 2 DOE DE-FG03-95ER45529

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Previous year's research:

The work in the past year has primarily involved four areas of magnetic thin films: amorphous rare earth-transition metal alloys, epitaxial $CoPt_3$ and Ni-Pt alloy thin films, amorphous rare earth doped Si (a new class of dilute magnetic semiconductor with large negative magnetoresistance which we have discovered), and exchange-coupled antiferromagnetic insulators.

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, as originally described in the grant proposal. 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. In addition to magnetic measurements, we used small angle neutron scattering and our unique specific heat measurements to characterize these materials. These measurements have shown clearly that the properties of (Gd, Tb, Dy)-Fe (relevant to industrial use as a magneto-optic medium) are dominated by local structural coherence, causing these alloys to behave magnetically more like crystalline ferrimagnets than the spin-glass-like materials to which they are theoretically related, independent of the amount of macroscopic anisotropy. Introduction of Ni reduces the exchange sufficiently and frustrates the local structural coherence such that the materials appear spin glass like. This work formed half of a graduate student's completed PhD thesis and will be submitted for publication shortly.

The work on the epitaxial Co-Pt (and more recently 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. We have discovered that these alloys exhibit a remarkable new phenomena; a surface-induced miscibility gap in a material which is believed to be completely miscible in

the bulk. Growth-induced *immiscibility* in systems which are *miscible* in the bulk (as we are suggesting for Co-Pt) has not been previously observed in any material, making its origin an intriguing materials science question. We have shown that this miscibility gap is 100% correlated with the perpendicular anisotropy. Co-Pt alloys have been extensively studied for a wide variety of purposes, ranging from magnetic and magneto-optic properties (it was for a long time the best hard magnet at room temperature, and is currently under consideration as a magneto-optic recording media), to the possible use as a catalytic agent, to basic studies of its phase diagram, which includes an order-disorder transformation at high temperatures, and the importance of magnetic interactions in determining the phase diagram. The discovery that in thin film form, it is immiscible, leading to tiny oriented regions of Co-rich and Pt-rich material, is completely unexpected. We have recently shown that Ni-Pt exhibits the same phenomena. A crucial question which remains: are we truly probing a surface equilibrium phase, or is this a question of kinetic growth effects. We are currently completing measurements on the Ni-Pt alloy system, as well as some deposition rate tests to separate the role of kinetics and thermodynamics, and will then submit a long paper for publication. The work on $CoPt_3$ appeared in Physical Review Letters and has been the subject of several invited talks, including a March APS meeting and a Harvard University Physics Dept. Colloquium. It was the basis for a student's PhD thesis.

We are currently involved in several collaborations to measure specific heat of magnetic thin films, a measurement made possible by our unique microcalorimeters. Working with Ami Berkowitz in the Center for Magnetic Recording Research, we used the specific heat to study antiferromagnetic superlattices, specifically NiO (T_{Neel} = 525K), CoO (T_{Neel} = 295K), and MgO (non-magnetic) in various combinations to allow separation of effects of finite layer thickness and exchange coupling on the magnetic ordering. The problem of exchange coupling in multilayers impacts many of the current research areas in magnetism. Antiferromagnets are in some ways the cleanest systems in which to study these effects. NiO/CoO multilayers can be prepared with coherent interfaces, and have been previously shown by neutron scattering to be magnetically coherent across many layers, even above the Neel temperature of the CoO. Magnetization measurements of antiferromagnetic thin films 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 thin film; 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 results on the NiO/CoO show clearly the transition from a single transition temperature to two distinct transitions with increasing thickness of the individual layers. The results on the NiO/MgO and CoO/MgO multilayers show reductions in T_{Neel} as expected from finite size effects. These reductions however are far smaller than those shown in a recent Phys. Rev Lett from another group, and suggest difficulties with either their materials or the use of magnetization measurements for determining T_{Neel} for thin antiferromagnetic materials. This work was presented in an invited talk at the MMM conference. A paper on this has been submitted to Phys. Rev. Lett.. This work together with the specific heat measurements of the *a*-RE-TM alloys, were a student's PhD thesis.

Most recently, we have found a new giant magneto-resistive material, amorphous rare earth silicon alloys near the metal-insulator transition. Negative magnetoresistance of up to two orders of magnitude has been observed already, with indications of the possibility of larger values in related materials. While this material is at present not of significant practical value (the magnetoresistance vanishes above 50K and requires large fields), we have some ideas on how to improve these characteristics. Even if never practical, there is fundamental interest in the relationship between magnetization and electrical transport in systems such as this where enormous changes in transport properties result from magnetization changes. A paper on this work has been submitted to Phys. Rev. Lett.

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 use and for materials where anisotropy is an unwanted feature (for soft magnetic materials). The work on anisotropy in amorphous rare earth-transition metal alloys and on Co-Pt and related alloys will be continued with two approaches. First, we are in the process of setting 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. Our theory is that the perpendicular anisotropy in both materials is a consequence of surface energy minimization. For both materials, annealing leads to an isotropic structure. There is therefore a competition between achieving sufficient surface atomic mobility to allow the surface-induced anisotropy to develop and a relaxation of this anisotropy due to annealing which occurs as the film is grown at elevated temperatures.. We believe therefore 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. Very generally, we will use the ion mill to differentiate between issues of thermodynamics and kinetics in thin film growth processes.

The second area of planned work on the Co-Pt alloys involves changing compositions, both within the Co-Pt alloy system and with other Co-X alloys. There is still no theory of *why* the immiscibility occurs at the surface of $CoPt_3$. We have developed tentative hypotheses involving either surface segregation of Pt or enhanced magnetic moments of thin Pt layers in proximity to Co, but need other materials to test these.

We intend to continue exploration of these new amorphous magnetoresistance materials. There are several promising directions of new related materials. 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 fabricating a "scaled-down" version of our present devices which will allow measurements of individual layers less than 100Å thick.

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	08/01/92-07/31/97	2	UCSD
DoE	Growth induced magnetic anisotropy in amorphous thin films	$85,000/yr	11/01/94-10/31/97	1	UCSD
NSF	Focus group on highly correlated electron systems	$375,000/yr (for 7 P.I.s)	07/01/94-06/30/97	1	UCSD
NSF	Development of instrumentation for microcalorimetry of biological systems	$86,507/yr	10/01/95-09/30/98	1	UCSD

Pending:

Supporting Agency	Project Title	Award Amount	Period Covered	Man-Months CAL/ACAD/SUM	Location
NSF	Acquisition of instrumentation for a machine shop of the 21st century	$414,458/yr (Infrastructure)	09/01/95-08/31/98	1	UCSD

Publications:

P.W. Rooney, A. L. Shapiro, M. Q. Tran, and F. Hellman, "Evidence of a surface-mediated magnetically induced miscibility gap in vapor-deposited $CoPt_3$". Phys. Rev. Lett. **75**, 1843 (1995).

P. W. Rooney, PhD thesis, "Chemical and Magnetic Order in Vapor Deposited Metal Films", Sept. 1995.

E. N. Abarra, PhD thesis, "Heat Capacity Measurements of Magnetic Thin Films", Dec. 1995.

P.W. Rooney, A. L. Shapiro, M. Q. Tran, and F. Hellman, "Chemical and magnetic order in vapor-deposited $CoPt_3$ and $NiPt_3$". In preparation (for Phys. Rev. B).

E. N. Abarra, K. Takano, A. E. Berkowitz, and F. Hellman, "Thermodynamic Measurements of Magnetic Ordering in Antiferromagnetic Superlattices", submitted to Phys. Rev. Lett.

M. Q. Tran, A.E. Gebala, E. Wilcox, and F. Hellman, "Metal-Insulator Transition and Giant Magneto-resistance in Amorphous Magnetic Rare Earth-Silicon Alloys", submitted to Phys. Rev. Lett.

E. N. Abarra, A. L. Shapiro, M. Q. Tran, and F. Hellman, "Magnetic Ordering in Amorphous Rare Earth Transition Metal Thin Films", in final preparation, to be submitted to Phys. Rev. B

Presentations:

"Magnetically-induced miscibility gap in vapor-deposited single crystal $CoPt_3$ films", P. W. Rooney, M. Q. Tran, A. L. Shapiro, F. Hellman, March APS meeting 1995.

"Heat capacity measurements of *a*-$TbFe_2$ thin films", E. N. Abarra, A. L. Shapiro, K. J. Allen, M. Q. Tran, F. Hellman, March APS meeting 1995.

Invited talk: E. N. Abarra "Heat Capacity Measurements of NiO/CoO Superlattices", Magnetism and Magnetic Materials (MMM) Conference, Philadelphia, Nov. 1995.

"Surface-induced miscibility gap in vapor-deposited $Co_{1-x}Pt_x$ films", M. Q. Tran, A. L. Shapiro, P. W. Rooney, and F. Hellman, Magnetism and Magnetic Materials (MMM) Conference, Philadelphia, Nov. 1995.

Invited talk: F. Hellman "Growth-surface-driven immiscibility in Co-Pt and Ni-Pt alloy thin films", APS March meeting 1996.

Other invited talks on DOE-supported research: (F. Hellman)
"Randomness and order in amorphous and crystalline thin films"
Tulane University Colloquium, Feb. 3, 1995.
Harvard University Physics Dept. Colloquium, March 11, 1996
U. Alabama, Tuscaloosa, Colloquium, May 25, 1996
"Evidence for a Magnetically-Driven Miscibility Gap in Co-Pt Thin Films",
UCIrvine May 8, 1995.
UCBerkeley condensed matter seminar Nov. 29, 1995

"Magneto-transport and Metal-Insulator Transition in amorphous RE-Si alloys", M. Q. Tran, E. M. Wilcox, A. E. Gebala, and F. Hellman. March APS meeting 1996.

"Surface-induced clustering in vapor deposited $Co_{1-x}Pt_x$ and $Ni_{1-x}Pt_x$ films", A. L. Shapiro, P. W. Rooney, M. Q. Tran, and F. Hellman, submitted to Magnetism and Magnetic Materials (MMM) Conference, Atlanta, Nov. 1996.

"Giant magneto-resistance in amorphous rare earth silicon alloys", M. Q. Tran, E. M. Wilcox, A. E. Gebala, and F. Hellman, submitted to Magnetism and Magnetic Materials (MMM) Conference, Atlanta, Nov. 1996.

Personnel associated with program:

In addition to the Principal Investigator, there are currently two graduate students (Alex Shapiro and Dongkyun Kim) and an undergraduate involved with the research. A post-doc (Minh Tran) was also involved in this research and partially supported; he has recently taken an industrial position. Another graduate student (Peter Rooney) was supported from 11/94 - 2/95 while he completed his PhD research on anisotropy and order in epitaxial $CoPt_3$ thin films. Noel Abarra was also supported for his PhD research on heat capacity measurements on magnetic thin films.