Designing Nanoscale Materials Lecture Series by 2004 Debye Institute Professor Christopher B. Murray

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Debye Lecture 6

Nanostructured Magnetic Materials for Information Technology C. B. Murray

Magnetic Nanocrystals and Nanocrystal Superlattices

Inorganic Core 1-15nm



Surfactants 1-4 nm thick

(4)



C.B. Murray, S. Sun, F. X. Redl, K. S. Cho and W. Gaschler.

IBM T. J. Watson Research Center; Yorktown Heights, NY

- (1) Synthesize, characterize and integrate nanostructured materials.
- (2) Probe the limits conventional materials/device scaling.
- (3) Harness mesoscopic properties for future technology.
 - Explore the potential of self-assembly for nanofabrication.



Film Growth: Self-Assembly



Nanocrystal Superlattice



Annealed Superlattice



Patterning & addressing



Applications & Opportunities for High Energy Product magnets.



Micro/Nano Devices





Automotive and Avionic Components



Medical diagnostic system





Hard disk drives Head actuators Various actuators in acoustic systems



Advanced Technologies To Delay Superparamagnetism

1. AFC media - implemented 1Q2001

2. Perpendicular recording



Reduces demagnetizing influence of adjacent bit fields, minimizes transition parameter. Involves new head configuration, return path soft underlayer, as NiFe, in media.

3. Reduce BAR (Bit aspect ratio) 20 ----> 4

super2001vt.cdr

4. Patterned media



5. Thermally assisted writing



Required because of increased media coercivity (increases Ku to compensate for a reduced V). Involves new magnetic materials

Ed Grochowski at Almaden



a dvrdmp21 a.prz

ED GROCHOWSKI at ALMADEN

Superparamagnetism



Orientation







Magnetization - size dependence



10nm fcc-Co particles

2-2.5nm fcc-Co particles





Areal Density of Magnetic HDD and DRAM





Read Head Design Technologies





Ed Grochowski af Almaden

Flojected IBIM MR/GIMR Read Read Evolution

Year	Areal Density Gbits/in ²	Product	MR/GMR Sensor 4.5 µm
1991	0.132	Corsair	
1992 1993	0.260 0.354	Allicat Spitfire	64 nm
1994	0.578	Ultrastar XP	
1995	0.829 0.923	Ultrastar 2XP Travelstar 2LP	
1996	1.32 1.45	Travelstar 2XP Travelstar VP	
1997	2.64 2.68 3.12	Travelstar 5GS <mark>Deskstar 16GP</mark> Travelstar 8GN	
1998	3.74 4.1 5.7	Travelstar 6GT Deskstar 25GP Travelstar 6GN	Transition 0.5μm
1999	5.3 10.1	Deskstar 37GP Travelstar 18GT	Contacts
2000	7.04 14.5 17.1	Ultrastar 36LZX Deskstar 40GV Travelstar 30GT	Exchange Hard Bias NiFe
2001	13.2 25.7	Ultrastar 73LZX Travelstar 30GN	Soft Film GMR Pinned 12 nm
2002	>30 >60		Film \$

Super2000aa.cdr

Evolution of Magnetic Read/Write Sensors

Ferrite Inductive MnFe

Machined Pole Pieces

Gap Width Controlled

By Films And Assembly

Read/Write Head

Wire wound coil

Tolerances

Thin Film Inductive Write MR Read Head Write Wide-Read Narrow Four Contact Structure SAL NiFe MR Film

0

0

Tunnel Junction Read Head

0

CPP Operation

Thin Film Inductive Read/Write Head Coil, Pole Geometries Controlled By Semiconductor Type Process NiFe Poles

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Thin Film Inductive Write GMR Read Head Write Wide-Read Narrow Four Contact Structure Pinned, Free Films Antiferromagnetic Exchange Film CIP Operation



Physical spacing and disk surface evolution





ED GROCHOWSKI at ALMADEN

ibim fibb besign filojections

Server	Server 3.5 Inch HDD 25.4 mm high		2000	2002	2004	2006
25.4 mm high			73 GB 10000 RPM 4.9 ms Tseek	73 GB 15000 RPM 4.0 ms Tseek		
Entry-Server 3.5 Inch HDD 25.4 mm high		37 GB 7200 RPM 8.5 ms Tseek	75 GB 7200 RPM 8.5 ms Tseek	144 GB 10000 RPM 7.0 ms Tseek	300 GB 10000 RPM 4.0 ms Tseek	600 GB 15000 RPM 3.0 ms Tseek
Mobile 2.5 Inch HDD 9.5/12.5mm high		25 GB 5400 RPM 12 ms Tseek	36 GB 5400 RPM 10.0 ms Tseek	50 GB 5400 RPM 9.0 ms Tseek	100 GB 7200 RPM 7.0 ms Tseek	200 GB 7200 RPM 5.0 ms Tseek
Consumer 1.0 Inch HDD 5.0 mm high		0.34 GB 4500 RPM 15 ms Tseek	1.0 GB 3600 RPM 15 ms Tseek	2.0 GB 3600 RPM 15 ms Tseek	4.0 GB 4500 RPM 12 ms Tseek	8.0 GB 4500 RPM 10 ms Tseek





IBM

Fullerton, E. et. al., Appl. Phys. Lett., 77, 3806, 2000

Synthesis and Self-assembly of Co nanoparticles

- High temperature (200 °C), solution phase synthesis.
- Rapid nucleation growth controlled by coordinating ligands.
- Size distribution improved by size selective precipitation.



Synthesis of Transition Metal Nanocrystals





Co 8 nm

Ni 9 nm

Co/Ni 9 nm

Crystal phases of Cobalt

3 crystal phases are studied..

(3) E-Co



Fcc and hcp differ only in stacking sequence of close-packed layers.

fcc: ABCABC...

Hcp: ABABAB...



Cubic unit cell
Complex internal structure
Set I - 8 atoms
Set II - 12 atoms

Dinega, D.P; Bawendi, M.G. Angew. Chem., 1999, 38(12), 1788.

XRD modeling of cobalt nanoparticles

- Better fits obtained by including
 - Stacking faults
 - Twin faults
- Introduction of stacking faults generates mixed fcc/hcp structures.
- Leads to the inter conversion of fcc and hcp phases





XRD Modeling of hcp nanoparticles



- TEM images show that hcp Co nanoparticles are slightly prolate.
- XRD fitting show extensive faulting/disorder.
 - Approximately one fault every 2.5 stacking planes.
 - Consistent across a variety of particle sizes.



XRD Modeling of fcc nanoparticles





- TEM images show that fcc Co nanoparticles are spherical in shape.
- XRD fitting one fault every 4 planes.
 - Bad fits at higher angles.
- Dark regions in TEM imply "multiple twinned" (MT) structures.



XRD Modeling of MT polyhedra

- Better fits have been reported for MT polyhedra
 - Highly faceted structures
 - Icosahedral, cubeoctahedral and decahedral structures suggested
- HR-TEM images also suggest the presence of multiple domains
 - Consistent with multiple twinning





Decahedron

Cubeoctahedron Icosahedron



Hall,B.D. et al., Phys. Rev. B, 1991, 43(5), 3906.

XRD Modeling of ε-Co nanoparticles





- TEM images show that ε-Co forms as spherical nanoparticles with narrow size distributions.
- XRD fits perfect crystalline internal structure.
- Supported by HR-TEM images of individual nanoparticles.

Modeling of the magnetization of Co nanoparticles

•Equilibrium partition function of nanoparticles in applied magnetic field. $< M >= \int dKp(K) \int dVp(V) \int dH_{\theta} \int dH_{\varphi} \frac{\int d\mu_{\theta} \int d\mu_{\varphi} M_{sat}(\hat{\mu} \bullet \hat{H}) e^{-E(\hat{H},\hat{\mu},K,V)/k_{B}T}}{\int d\mu_{\theta} \int d\mu_{\varphi} e^{-E(\hat{H},\hat{\mu},K,V)/k_{B}T}}$ $E/V = -M_{sat} \hat{\mu} \bullet \hat{H} - KS_{z}^{2}$

 $M_{rem}(t) = \int dK p(K) \int dV p(V) \left[\alpha M_{sat} e^{-t/\tau} \right] \text{ where } \tau = \tau_o e^{-KV/k_B T}$



Magnetic modeling of MT Co nanoparticles



- TEM analysis 7 nm diameter
- Magnetic fitting
 - Diameter 6.2 ± 0.5 nm
 - K $7.0 \times 10^5 \pm 3.5 \times 10^5 \text{ ergs cm}^{-3}$
- Smaller "magnetic" diameter accounted for by the presence of oxide layer.
- Anisotropy close to bulk fcc value
- Remnant magnetization is half saturation magnetization at low temperatures
 - Implies uniaxial symmetry.

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- Remnant magnetization is half saturation magnetization at low temperatures
- Implies uniaxial symmetry
 - Predicted for MT polyhedra

Magnetic modeling of ϵ -Co nanoparticles



- TEM analysis diameter of 9.5 nm
- Magnetic fitting
 - Diameter 8.4 ± 0.9 nm
 - Anisotropy $7.1 \times 10^5 \pm 4.0 \times 10^5 \text{ ergs cm}^{-3}$
- Anisotropy also close to bulk fcc value
- Remnant magnetization is half saturation magnetization at low temperatures
 - Implies uniaxial symmetry.



Materials Selection: K_uV >> kT



CoPt L1₀ structure (tetragonal)

Shape ?
Solution phase synthesis



H₃C

CH3



Nanoparticles for magnetic storage

- Narrow size distribution bigher thermal stability
- Smaller particles
 marrower transition widths

 $\begin{array}{l} \textbf{35 GBit/in^2 prototype media} \\ \textbf{8.5 nm grains} \\ \sigma_{area} \, \widetilde{=} \, \textbf{0.6} \end{array}$

Nanoparticle arrays 4 nm FePt particles $\sigma_{area} \cong 0.05$



S. Sun, Ch.Murray, D. Weller, L. Folks, A. Moser, Science, 287 (2000) 1989

Magnetic properties

• Annealing leads to formation of ordered, ferromagnetic phase



Chemically disordered fcc structure Superparamagnetic



Pt 🔘 Fe

Annealing at 550C



Chemically ordered fct structure Ferromagnetic



Magnetic properties

Order parameter and coercivity increase with annealing temperature and duration
 3 layer samples of 6 nm FePt particles



XRD data M. Toney, IBM Almaden

VSM Hysteresis loops

3 layers, annealed in N₂ at 580 C for 30 min, FePt samples from $FeCl_2$



Chemical analysis

• Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy shows iron oxide fraction that is reduced upon annealing



Special thanks to Robin Farrow for providing iron oxide reference samples.

Structural properties



TEM images of 6 nm particles (a) as synthesized (b) 530 °C for 60 min in vacuum (c) 600 °C for 60 min in vacuum

TEM images courtesy of Zu-Rong Dai

 X-ray scattering and TEM used to study structural properties
 3 layers of 4 nm particles annealed in N₂

XRD data M. Toney, IBM Almaden



Polymer-mediated self assembly

- Substrate surface is functionalized
- Dipped into dispersion of stabilized nanoparticles
- Ligand exchange leads to formation of strongly bound layer of nanoparticles
- New layer of functional molecule replaces stabilizer
- Repeat process to form multilayers



S. Sun, C. B. Murray, IBM Yorktown

Magnetic recording



Size control of nanocrystals in the absence of Ostwald ripening



Factors influencing the nucleation rate

- reaction temperature
- concentrations of precursors
- concentrations of surfactants

CoPt₃ nanocrystals



30 nm

Fe₂O₃ nanocrystals



– 20 nm



Cobalt Nanocrystal Superlattices (T. Betley et al)



Hexagonal packing

10 nm Cobalt NCs

Cubic packing

Three-dimensional colloidal supercrystals of CoPt₃ nanocrystals





Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany









For the unannealed particles the ratio in the spectra can be estimated as 20% Fe, 80% Fe2O3 (I am still not sure what oxide we have, maybe a mixture). On the left is the contribution to the spectra as a function of radius. A 3nm diameter FePt metal core with a 0.5nm thick oxide shell would produce such a spectrum.





energy (eV)

For the annealed particles the metal ratio is much higher, here an example for 650C/5min anneal. On the left is the contribution to the spectra as a function of radius. A 3.6 nm diameter FePt metal core with a 0.2nm thick oxide shell would produce such a spectrum.



total electron yield (rel. units)



L3



along easy axis run 20125013

Polar Kerr







Fe3O4 sample from Robin XMCD in 500 Oe, 20 degrees incidence along easy axis test reproducibility - is very good

Three layers of PEI-E066 on Si(110) annealed under Ar + H(5%) for 30 min. The samples have been immersed into acetone for 1 min and dried. 030902-A, 400C 030902-B, 450C 030902-B, 450C 030902-C, 500C 030902-D, 530C 030902-E, 560C 030902-F, 580C







And here the comparison between 8nm, 6nm, and 4nm.



energy (eV)





From Mike Toney, XRD



From Mike Toney, XRD



Hello,

Here the data from the latest ALS run. Jan made two samples for comparison, sample #4 is 50 nm Fe55Pt45 without cap layer sample #5 is 50 nm Fe55Pt45 with 2 nm Pt cap layer Here the Fe spectra for comparison. The one without cap layer is much more oxidized as expected.



This graph shows sample #5 with respect to a clean Fe reference, and the best fit to the spectrum I got with assuming 70% Fe and 30% FeO.



And the contribution to the spectra of Fe and Fe3O4 for 8nm, 6nm, and 4nm. If I put this into the model the oxide layer for the 6 and 8 nm particles seems to be thinner (2A) than for the 4 nm particles (4A).



particle size (nm)



6nm

8nm

The 8nm sample has very high coercivity.

041801-E	E098, 6nm Fe ₅₂ Pt ₄₈	SiO ₂ /Si	PEI-E098, 7Layers	N ₂ , 580C, 30 min
041801-F	E095, 8 nm ~Fe ₅₂ Pt ₄₈	SiO ₂ /Si	PEI-E095, 7Layers	N ₂ , 580C, 30 min

This is a comparison of the films made 030101. They are all just after the onset of being ferromagnetic, the spectra are all very similar.



energy (eV)





030101-A	E066, Fe ₅₈ Pt ₄₂	SiO ₂ /Si	PEI-Fe ₅₈ Pt ₄₂ , 2 layer	N ₂ , 580C, 30 min
030101-В	E066, Fe ₅₈ Pt ₄₂	SiO ₂ /Si	PEI-Fe ₅₈ Pt ₄₂ , 2 layer	N ₂ , 580C, 30 min
030101-C	F062, Fe ₅₀ Pt ₅₀	SiO ₂ /Si	PEI-Fe ₅₀ Pt ₅₀ , 3 layers	N ₂ , 580C, 30 min
030101-D	F070, Fe ₅₅ Pt ₄₅	SiO ₂ /Si	PEI-Fe ₅₅ Pt ₄₅ , 3 layers	N ₂ , 580C, 30 min
030101-E	E068, ~8nm FePt	SiO ₂ /Si	PEI-FePt, 1 layer	N ₂ , 580C, 30 min

Hi all,

I did a calculation of the signal one would expect in total yield detection for the following geometry:

This is basically a particle of 40A diameter with 32A FePt core surrounded by one monolayer Fe3O4. It is embedded in the polymer (for the calculation I assumed just carbon) with 60A particle distance, that gives about 10A carbon on top.



Synthesis and Characterization of Iron Oxide Nanoparticle



Fe3O4 Nanocrystals

(Sun and Zeng)

Fe(acac)₃ + ROH + RCOOH + RNH₂ + Ph₂O

Figure 1. TEM bright field image of 16-nm Fe₃O₄ nanoparticles deposited from their dodecane dispersion on amorphous carbon surface and dried at 60 °C for 30 min: (A) a monolayer assembly, (B) a multilayer assembly,

(C) HRTEM image of a single Fe₃O₄ nanoparticle. The images were

acquired from a Philips EM 430 at 300 KV.



Shape selective synthesis of wuestite



FeO Nanoparticles



Right a) TEM image of a single cubic superlattice built of cubic FeO nanocrystals with 11 nm edge length. b) TEM image of a larger superlattice oxidized or decomposed after storage. c) SAED of the cubic superlattice in b) showing reflections for magnetite and orientational ordering in the superlattice.

Right: a) LRTEM image of a quadratic subunit of a TEM grid showing nearly cubic superlattice built up of cubic wuestite nanocrystals. b) SAED of a selected superlattice with uneven but symmetric intensity distribution caused by preferred alignment of the particles (orientational ordering). c) TEM image of aligned superlattices arising during deposition of cubic FeO nanocrystals in a magnetic field parallel to the substrate. d) TEM image of aggregated superlattices deposited without external magnetic field.


Figure 6: a) TEM image of wuestite nanocrystals with seeds of magnetite inside. b) SAED of the material showing a speckled pattern for FeO reflections and diffuse rings for magnetite reflections. c) Dark-field image of the region in Figure 5a (shown as negative); a part of the magnetite reflections were selected with the objective aperture. d) Dark-field image of the region in Figure 5a (shown as negative); a part of the wuestite reflections were selected with the objective aperture.





Sun et al, J. Am. Chem. Soc. 2004, 126, 273.

Shape induce crystal alignment

(14 nm MnFe₂O₄ nanoparticles)



H. Zeng, et al

Dark Field Imaging of the Fe3O4 and FeO in TEM.



Figure 6: a) TEM image of wuestite nanocrystals with seeds of magnetite inside. b) SAED of the material showing a speckled pattern for FeO reflections and diffuse rings for magnetite reflections. c) Dark-field image of the region in Figure 5a (shown as negative); a part of the magnetite reflections were selected with the objective aperture. d) Dark-field image of the region in Figure 5a (shown as negative); a part of the wuestite reflections were selected with the objective aperture.

Bimagnetic Core/Shell Nanoparticles



Figure 1. TEM bright field images of core/shell $Fe_{58}Pt_{42}/Fe_3O_4$ nanoparticles with core/shell being (A) 4 nm/0.5 nm and (B) 4 nm/2 nm; (C) HRTEM of a single $Fe_{58}Pt_{42}/Fe_3O_4$ particle with 4 nm core and 2 nm shell; and (D) EDX spectrum of a group of $Fe_{58}Pt_{42}/Fe_3O_4$ nanoparticles with 4 nm core and 1 nm shell. The shell thickness is measured statistically with standard deviation at around 11%.

Zeng et al, Nano Lett. 2004, 4, 187.



Spin-dependent tunneling in Nanocrystal arrays



shortest current path ~ 8 nanocrystals





data fit by: $ln(G_{V=0}) = const. - E_c/k_BT$ \triangleright from fit to data, measure $E_c \sim 10 \text{ meV}$

For all devices measured, 10 meV < Ec < 14 meV</p>





Fe3O4 Nanocrystals

(Sun and Zeng)

Fe(acac)₃ + ROH + RCOOH + RNH₂ + Ph₂O



Figure 1. TEM bright field image of 16-nm Fe_3O_4 nanoparticles deposited from their dodecane dispersion on amorphous carbon surface and dried at 60 °C for 30 min: (A) a monolayer assembly, (B) a multilayer assembly, (C) HRTEM image of a single Fe_3O_4 nanoparticle. The images were acquired from a Philips EM 430 at 300 KV.



Potential for spintronic device applications



Nanoparticle synthesis from self-assembled polymer templates

- Diblock
 copolymer
 system
 PS/PMMA
- Self-assembly promoted by heating
- Removal of PMMA



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