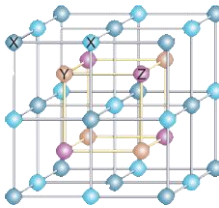
Heusler Compounds: CPP GMR, MRAM and making them by sputtering

Matthew Carey

Spin Transfer Technologies

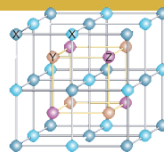


30 July, 2015

(very) Partial list of team members (IBM→Hitachi→HGST/WD)

- Bruce Gurney
- Jeff Childress
- Stefan Maat
- Jordan Katine
- Young-Suk Choi
- John Read
- Brian York
- Liz Brinkman
- Tomoya Nakatani
- Phil Rice (IBM)
- Andrew Kellock (IBM)

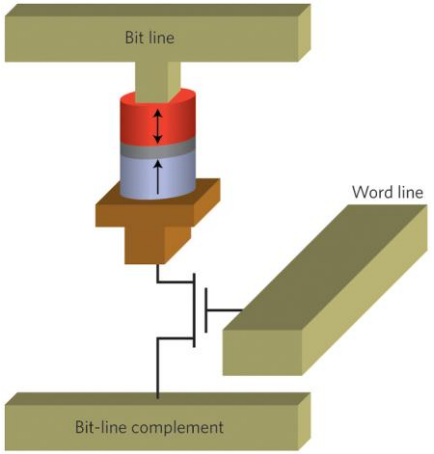
MRAM Basics



- MRAM: Magnetic Random Access Memory

- Memory stored in “free layer” magnetization
  - Written by Spin Transfer Torque

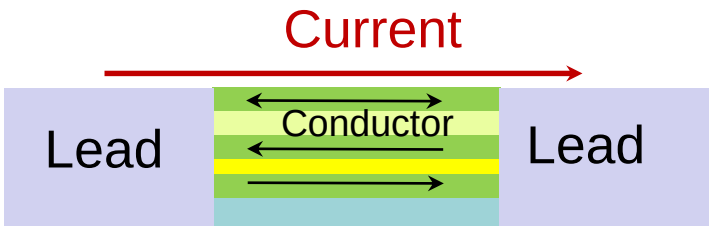
- Memory read by tunneling magnetoresistance (TMR)



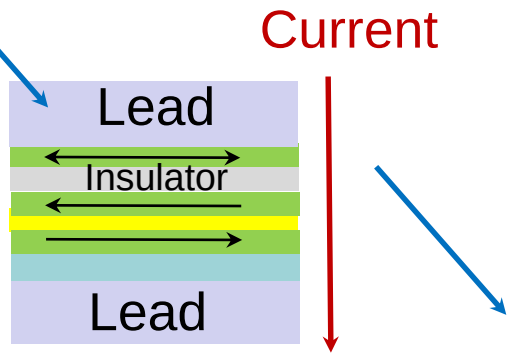
Kent and Worledge: Nature Nanotechnology 10, 187–191 (2015)

CPP-GMR Basics

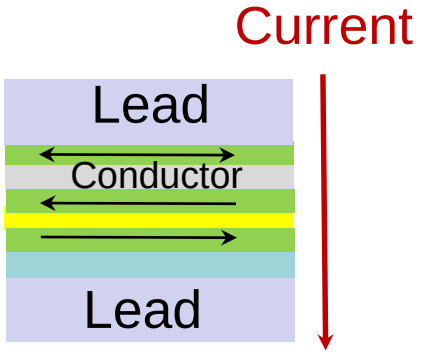
- CPP-GMR: Current Perpendicular to the Plane Giant Magnetoresistance
- Possible replacement for TMR (Tunnelling Magnetoresistance) read sensors



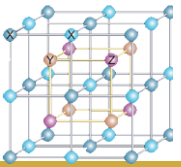
CIP GMR
(1998)



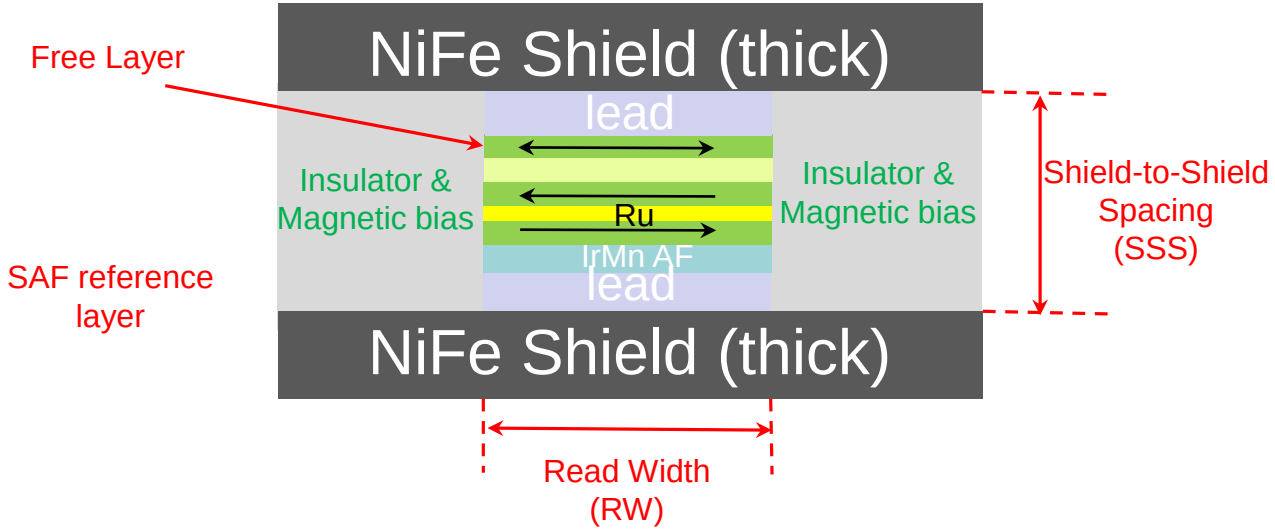
CPP TMR
(2005)



CPP GMR
(Future)

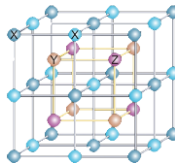


Anatomy of CPP-GMR read sensor

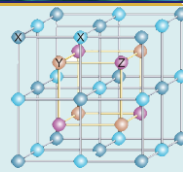


Magnetic layer thicknesses are *very* limited by head requirements

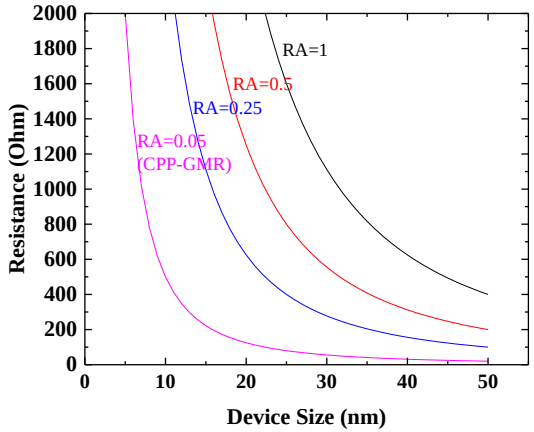
- Sensor resolution (density) is determined by RW and SSS
  - SSS limits overall stack thickness (@ 1TB/in^2, SSS<25nm)
- Read heads are flux sensors, not field sensors
  - Free layer moment must match flux from media
- Reference layer Stability limits magnetic moments
  - AF exchange coupling and RKKY coupling through Ru fall off as 1/moment



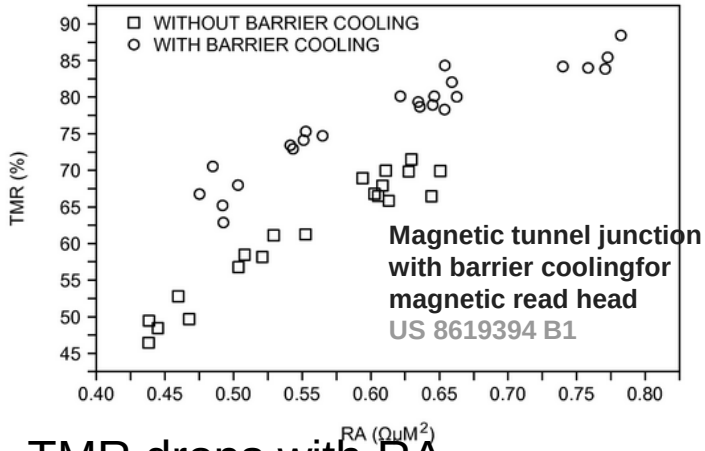
Why CPP-GMR?



- Big driving factor: Low RA
  - Qunwen Leng's presentation
  - As density increases, device size decreases
    - Resistance and Johnson noise increase
    - Requires low RA MTJ's
      - TMR descreases
      - Coupling fields increase
- GMR RA is about 0.05 Ω–μm^2



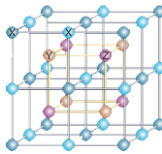
Resistance of square devices:
Climbing rapidly for RA>0.25



TMR drops with RA
→ Novel techniques to increase

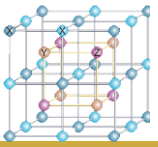
Heusler Compounds

- I prefer “compound” not “alloy”
- Discovered in 1903 by Friedrich Heusler
  - He mixed “nonmagnetic” Cu, Mn and Sn to get a magnetic compound
- In 1983 de Groot calculated that some Heusler’s could be half-metallic
- Heuslers are ordered compounds
  - Half Heusler: XYZ
  - Full Heusler: X_2YZ
- Chemically ordered → each atom has a specific location on the lattice

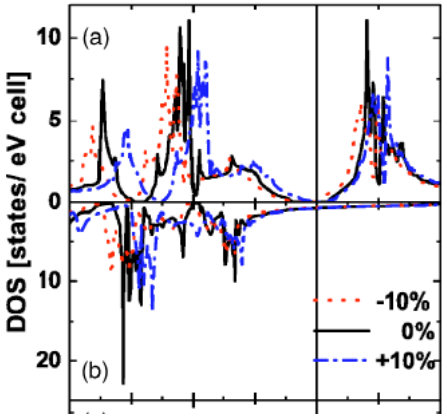


Half Metals

- Electrons with one spin direction are metallic.
  - No gap at Fermi energy
- Electrons in the other spin direction are semiconducting
  - Gap at Fermi Energy
- Polarization: $p=(n\uparrow-n\downarrow)/(n\uparrow+n\downarrow)$
  - Where $n\uparrow(n\downarrow)$ is the majority (minority) DOS at the E_{Fermi}.
  - Half metals have 100% spin polarization
  - ***Should* give infinite TMR or CPP-GMR**
  - **Low damping**
    - Lack of spin mixing channel
- Half metals are theoretically predicted
  - Zero temperature calculations
  - Real Heuslers are high spin polarization but perhaps not 100%
  - And that's OK—high polarization is good!
- Let me say this again:
  - **Low Damping**



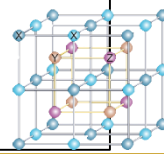
PHYSICAL REVIEW B 70, 205114 (2004)



NiMnSb Density of States (DOS)
Majority state (top): semiconducting
Majority state (bottom) metal
Shown with and without ±10% strain

Heuslers: advantages and challenges

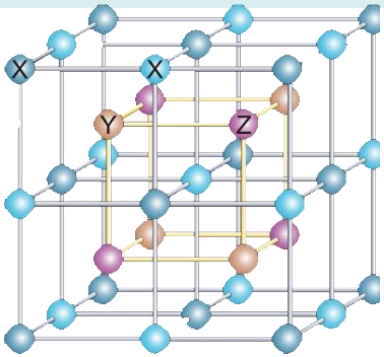
MRAM	CPP-GMR
Reduce Switching Current – High spin polarization (P) → highly susceptible to spin torque – Switching current proportional to damping $Jc_0 \propto \alpha$	Higher GMR – High spin polarization: $\Delta RA \sim 1 m\Omega - \mu m^2$ (std metal) $\Delta RA > 7 m\Omega - \mu m^2$ (Heusler) Most Heuslers are low anisotropy/in-plane magnetization
Most Heuslers are low anisotropy/in-plane magnetization	Low damping high P → Highly susceptible to spin torque
Must withstand 400ºC anneal Needs to be made thin	Anneal limited to <300ºC Needs to be made thin



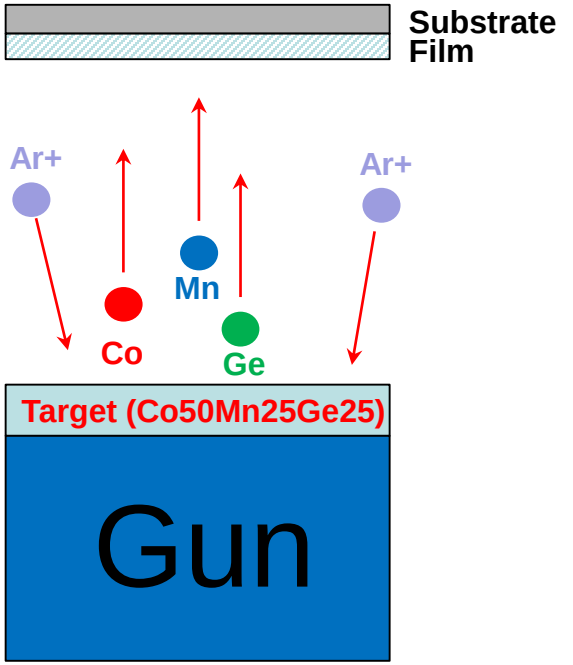
Compounds not alloys: Chemical ordering

- Each atom has a specific location on the lattice
  - $L2_1$ structure: true full Heusler
    - X_2YZ where X, Y and Z positions are clearly defined
  - B2 structure: X and Y can substitute, Z specified
    - B2 can give Half-metal band structure
  - It can be very hard to determine B2 vs $L2_1$
    - Consider Co_2MnGe and Co_2FeAl
      - $Z_{Mn}=25$, $Z_{Fe}=26$, $Z_{Co}=27$
      - I.e. very little contrast for XRD or TEM

$L2_1$ structure: X_2YZ
where X,Y and Z occupy specific sites on the lattice.
B2 has X and Y substitution

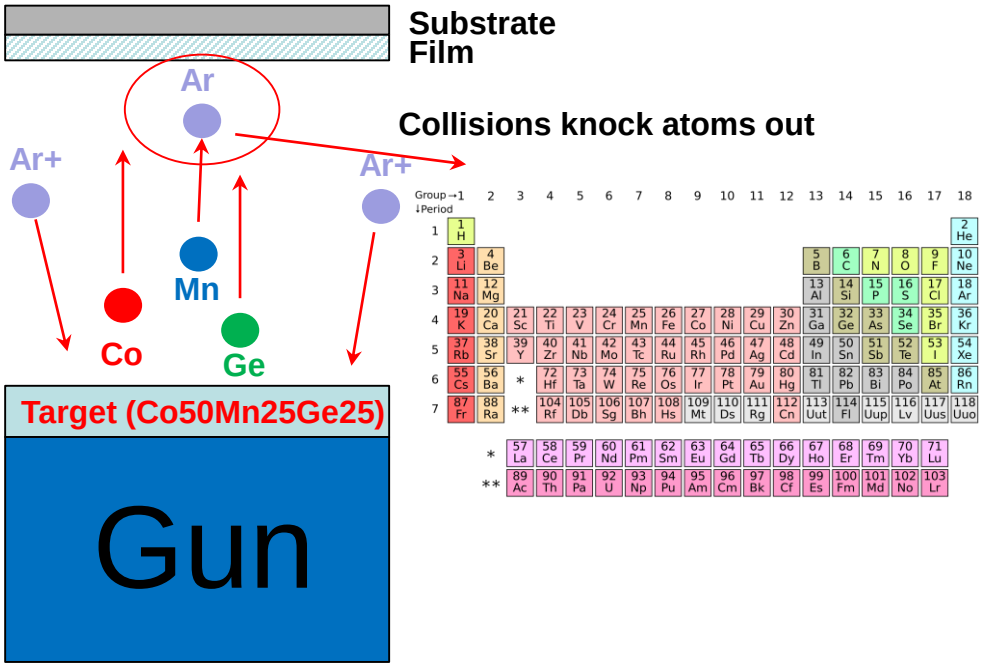


Sputtering: composition shift



Ideal case:
Ar ions hit target
Target atoms fly to substrate
→ Film composition = target composition

In real life film composition <> target composition



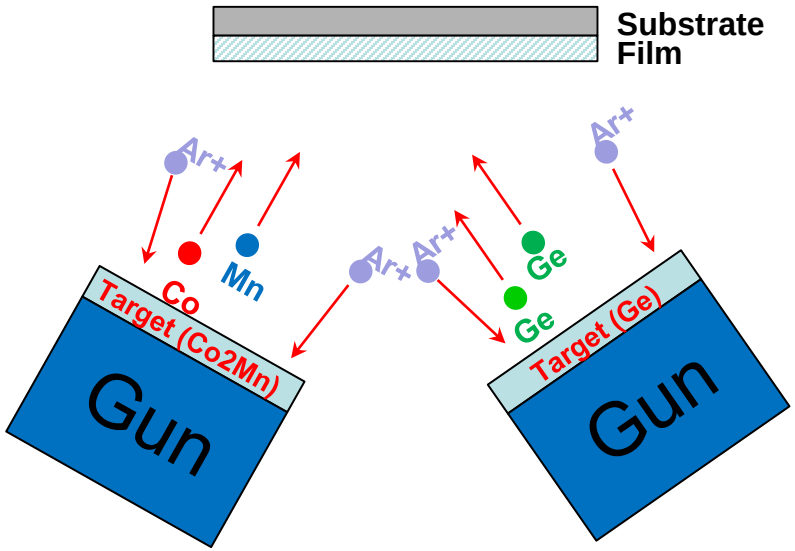
One reason for composition shift:
Gas phase scattering
  Pressure dependent (higher pressure → more shift)
Gas dependent
  billiard ball model
    when Mass(gas) ~ Mass(atom) → more scattering
    changing gas mass changes shift

Sputtering Heuslers: single target

- Most simple method: single target
  - Process flow:
    - Order target of desired Heusler composition
    - Test target composition
    - Order new target, adjusting for composition shift
    - Dial in composition, make films, do experiments
- I don't use this method: why?
  - Heusler targets were not available when I started
  - Heusler targets can be difficult to work with
    - Magnetic → targets be thinner → less utilization
    - Compounds → brittle → fragile
    - Less flexible than cosputtering

Cosputtering

- Sputter from 2 or 3 targets
  - e.g. Co_2Mn and Ge →Co_2MnGe
- Advantages?
  - Targets easier to manufacture
  - Targets are less fragile
  - Targets are thicker (0.25” vs. 0.125”)
  - Can vary “Z” element (X_2YZ)
    - E.g. Ge rich or Ge poor
  - Can easily change “Z” element
    - Change from Co_2MnGe → Co_2MnSi with a simple target change
    - Make quaternary: E.g. $Co_2Mn(Ge_xSi_{1-x})$ with three targets
- Things to watch out for
  - Mn targets can be brittle (>40at% Mn)
  - Mn is an oxygen getter
    - Mn alloy targets can have high oxygen content
    - Oxygen can make ordering more difficult
  - Pure Mn targets are difficult to obtain
    - Brittle
    - Oxygen contamination
    - Target can oxidize
  - Other targets can be difficult to make
    - E.g Ge-Ga (Ge and Ga do not alloy)



Example: using cosputtering to optimize Ge concentration

- Ge-rich $Co_2Mn\ Ge_x$ gave better GMR:
  - Co_2MnGe/Cu/Co2MnGe spin valve
  - Stochiometric Ge = 25%
  - GMR increases up to 28% Ge

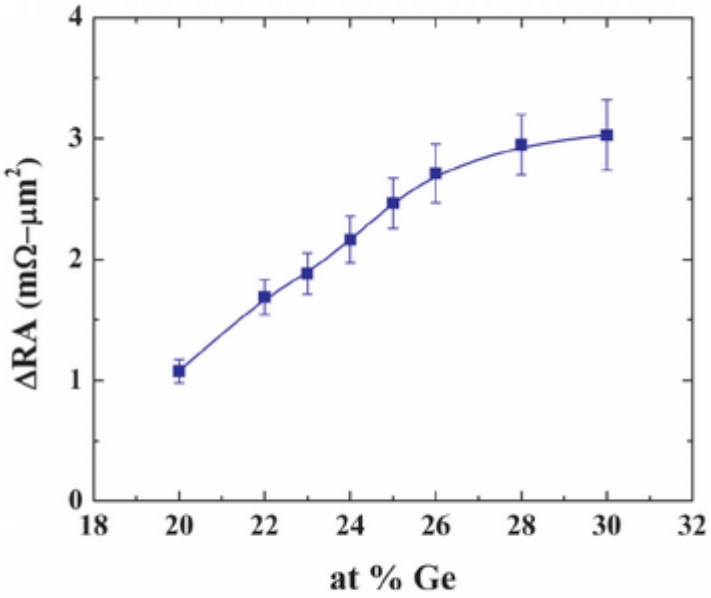


FIG. 7. (Color online) Δ*RA* versus Ge content for CPP spin valves with Co_2MnGe in the free and pinned layers. High GMR is observed throughout a broad range of compositions. Of particular note is the fact that the GMR is higher for Ge-rich CMG layers, which should show significant deviations from perfect order. Line is a guide to the eye.

JOURNAL OF APPLIED PHYSICS **109**, 093912 (2011)

Co_2MnGe-based current-perpendicular-to-the-plane giant-magnetoresistance spin-valve sensors for recording head applications

M. J. Carey,[a)] S. Maat, S. Chandrashekariaih, J. A. Katine, W. Chen, B. York, and J. R. Childress
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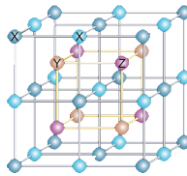
How to obtain chemical order?

Heated Substrates

- Optimize T_{sub} for order
- Films can be rough depending on underlayer
  - Poor wetting of surface
  - Interdiffusion

Post Deposition Anneal

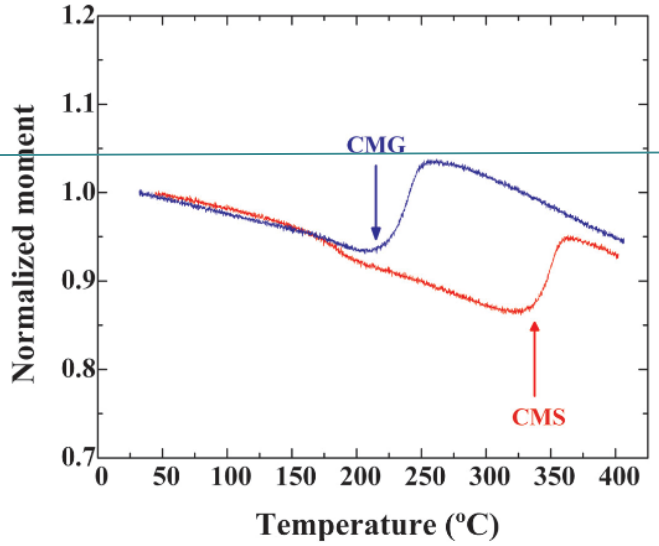
- Deposit disordered films
- Anneal to obtain order
  - In-situ or ex-situ anneal
- Allows for adjacent layers to be deposited at RT easily
- Favored method of CPP-GMR teams



Optimizing Anneal

- Each compound has a crystallization temperature (T_{cryst}) and a maximum temperature.
  - E.g. T_{cryst}(CMG) < T_{cryst}(CMS)
  - Moment and resistance track crystallization
  - Too high anneal T and Heusler decomposes
  - Pick the compound based on anneal temperature
    - Heads T≤300ºC
    - MRAM T≥400ºC

Tracking crystallization by moment



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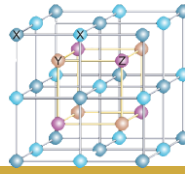
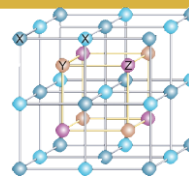
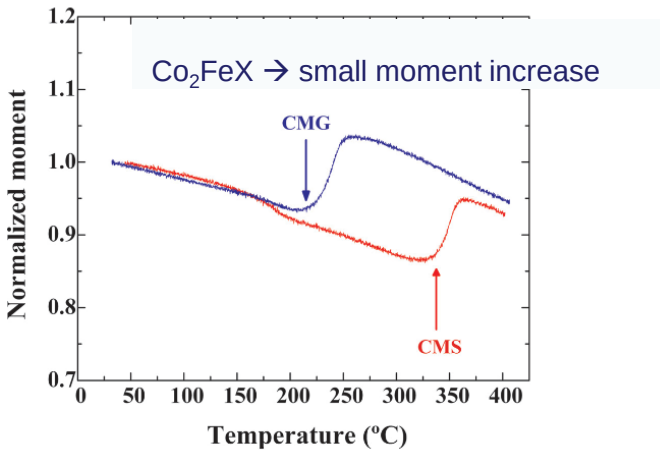
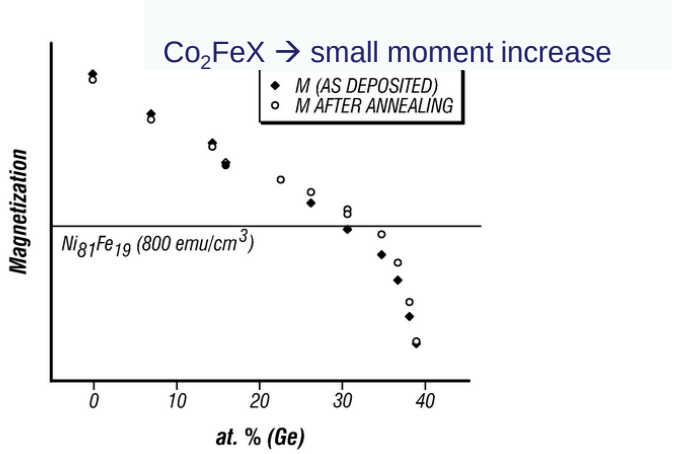


From a synthesis point of view each Heusler is different



- Co_2MnX alloys
  - Poorly crystallized as deposited
  - Large moment increases with anneal
- Co_2FeX alloys
  - Crystallized as deposited
  - On recrystallization, moment increase is small





Thin Heuslers. Or: Is my GMR dropping due to spin diffusion length or due to structure?

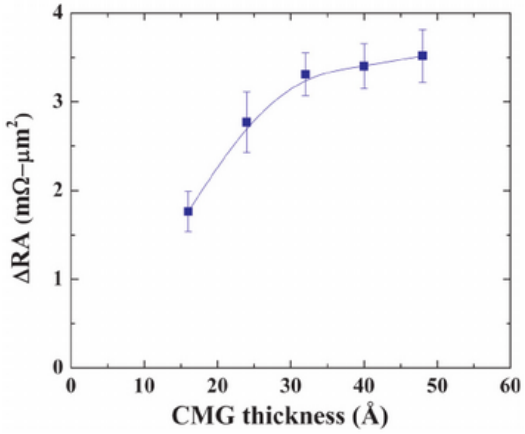


FIG. 8. (Color online) $\Delta R/R$ and ΔRA for simple spin valve with 32Å Co_2MnGe in the pinned layer and various thickness of Co_2MnGe in the free layer. Line is a guide to the eye. [Ta(50 Å)/Ru(20 Å)/IrMn(70 Å)/$Co_{65}Fe_{35}$(40 Å)/Ru(8 Å)/$Co_{50}Fe_{50}$(9 Å)/CMG28(32 Å)/$Co_{50}Fe_{50}$(5 Å)/Cu(40 Å)/$Co_{50}Fe_{50}$(5 Å)/CMG28(t Å)/$Co_{50}Fe_{50}$(5 Å)/Cu(200 Å)/Ru(50 Å)Ta(25 Å)].

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GMR drop off for thin CMG

Giant magnetoresistance in PtMn alloys

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Appl. Phys. Lett., Vol. 84, No. 16, 19 April 2004

TABLE I. Activation energy (E_a) in eV for 100, 150, and 200 Å thick PtMn films. E_a was calculated using two methods: time to reach 50% of total resistance change (t_{50}) and the slope of $\rho(t)$ at t_{50}, $d\rho/dt$.

Å	$E_a(d\rho/dt)$	$E_a(t_{50})$
200	1.54	1.45
150	1.54	1.60
100	2.09	1.82

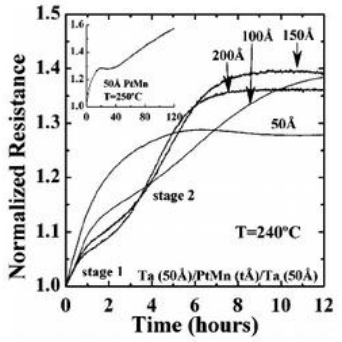


FIG. 4. Normalized resistance vs time for Ta/PtMn/Ta trilayers annealed at 240 °C. Inset shows a longer anneal at 250 °C for a trilayer with 50 Å PtMn.

Example:

Chemical ordering in (non Heusler) PtMn

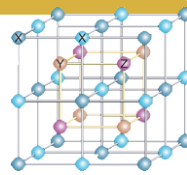
measured via resistance vs. time at anneal T

activation energy increases as t_{PtMn} decreases

Can I use the same recipe for thin Heusler films as for thick?

Answer: Don't count on it!

Optimizing Co_2MnX Heuslers



- Better GMR with amorphous layer under Heusler
  - Ta or CoFeBTa thin layers.
  - GMR increased from 3.5 → 5mΩ–μm^2.

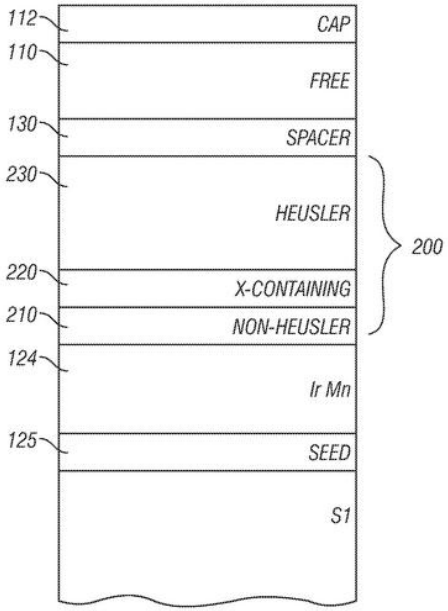


FIG. 5

Insert layer between crystalline seed and Co_2MnX

Current-perpendicular-to-the-plane (cpp) magnetoresistive sensor with multilayer reference layer including a heusler alloy

US 20130236744 A1

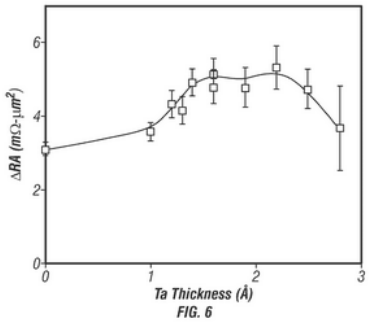


FIG. 6

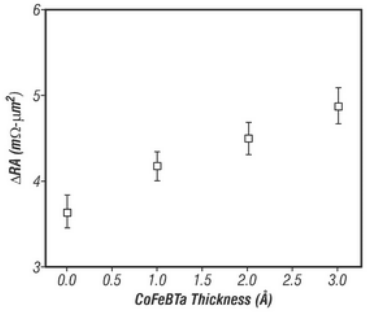
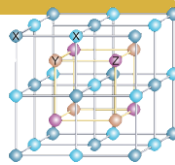


FIG. 7

GMR increases with amorphous layer thickness

Why does GMR increase?

- Chemical order as measured by XRD increases in annealed samples
  - Crystalline quality poor as-deposited
  - I.e. amorphous layer insert drives CMG more amorphous a deposited. But this allows for higher quality after anneal.



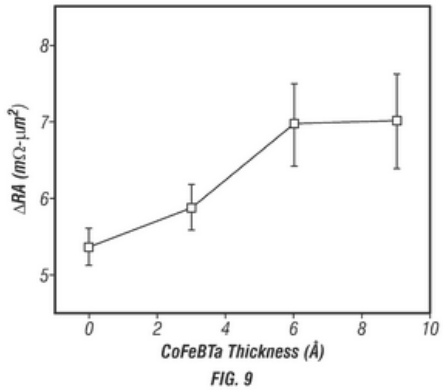


FIG. 9

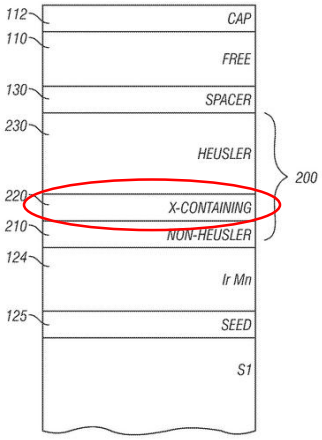


FIG. 5

- Max GMR is comparable to single crystal CMS data.

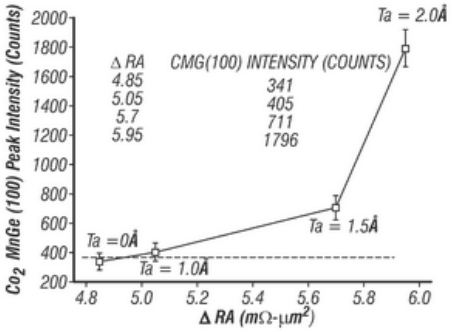


FIG. 10

- Superlattice peak (100) intensity increases with Ta thickness.

→ better chemical order in CMG when deposited nearly amorphous

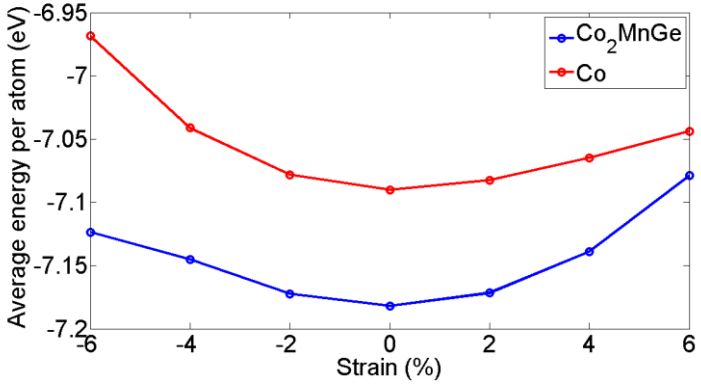
- GMR increases with (100) Peak intensity

Why does this increase chemical order?

1) Makes the Co_2MnX film amorphous as deposited
   1) Reduces activation energy for chemical order by combining chemical ordering with crystallization
   2) In-situ anneal with Heusler top surface free

   → Nothing to stress Heusler

2) Hypothesis: stress relief
   - Amorphous interlayer breaks epitaxy/reduces epitaxial stress
   - Groun tate increases with stress



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Perpendicular Heuslers: interfacial anisotropy

MgO can give iPMA

Seeds can give iPMA
use MgO, Pt, Pd, etc.

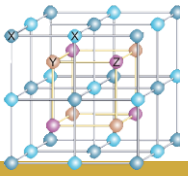
If cubic Heusler is thin enough (~1nm) and has surface anisotropy, one can obtain perpendicular magnetization (similar to CoFeB often used in MRAM)

But is it still a Heusler?

Very thin films hard to characterize

PMA inducing interface materials (Pt, Pd, etc) often increase damping which can negate advantage for MRAM

Interfacial PMA (like that from MgO) has a strong temperature dependence



Tetragonal Heuslers for perpendicular magnetization

"New" class of Heuslers

tetragonal crystal structure (D022)

→ allows for perpendicular anisotropy

High spin polarization (not full half metal)

High Anisotropy

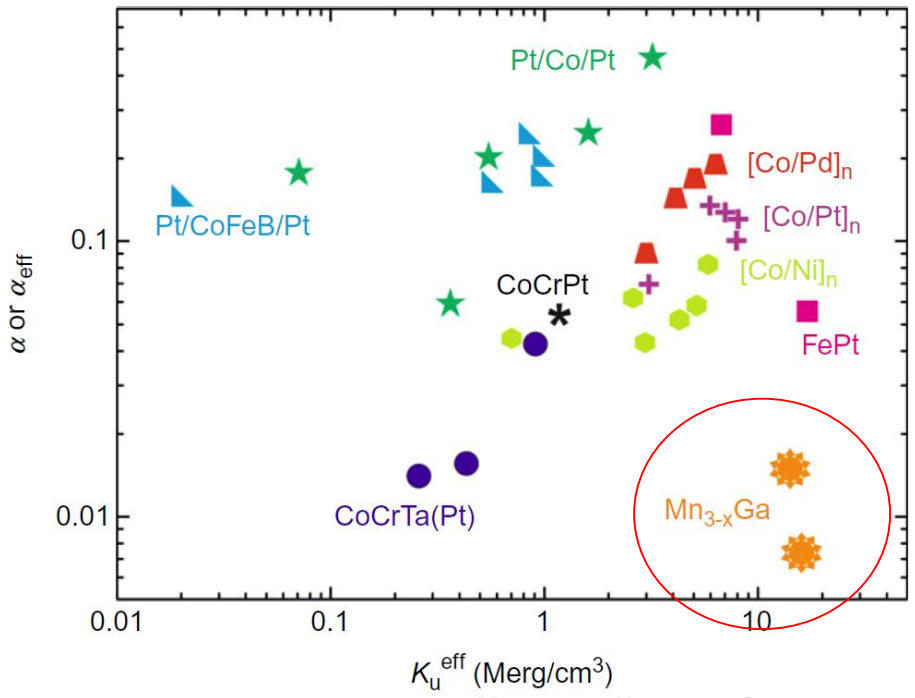
Low damping

The challenge and the future:

Learning how to make this in thin films

<5nm is tough

roughness



MAGNETIC HEUSLER COMPOUNDS

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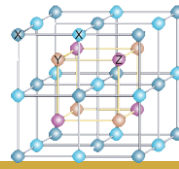

Summary

- Heusler compounds offer advantages for CPP-GMR and MRAM
  - High spin polarization (good for CPP-GMR)
  - Low damping (good for MRAM)
- The past challenge and the future is in fabrication
  - Especially true for thin films (<3nm)
    - Difficult to fabricate
    - Difficult to characterize
  - Each Heusler and each family have unique fabrication strategies
  - Perpendicular MTJ's present a further challenge

    →Perpendicular moment without compromising damping