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# **Nanostructures with perpendicular magnetic anisotropy**

**Applications:** 

Spintronic devices High density recording media Magnetic field sensors Magnetic tunneling junction sensors

# Scope of the talk

Correlation between morphology, structure and magnetic properties in two types of nanostructured films:

*I.* Composite metal-insulator films FeCo-CaF<sub>2</sub>, FeCo-Al<sub>2</sub>O<sub>3</sub>

*II.* Porous thin multilayered films of Co/Pd and Co/Pt



# **Investigation with complimentary techniques:**

**X-ray diffraction,** Empyrean PANalytical diffractometer, Cu  $K_{\alpha}$ 

Transmission electron microscopy, Philips EM400T microscope, 120 kV

High-resolution electron microscopy, Philips CM200, 200 kV

X-ray absorption spectroscopy (EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Structure) ranges), European Synchrotron Radiation Facility

<sup>57</sup>Fe Mössbauer spectroscopy, 77 K, 300 K, Co/Rh source, 40 mCi

**Vibrating sample magnetometer,** *Quantum Design PPMS, magnetic induction H up to 9 T, temperature T up to 2 K* 



#### Perpendicular magnetic anisotropy:

#### Easy axis magnetization pointing perpendicular to the films plane



# Experimental



# *I.* Composite metal-insulator films FeCo-CaF<sub>2</sub>, FeCo-Al<sub>2</sub>O<sub>3</sub>

- tunable magnetic and electric properties
- microminiature scale & arbitrary shape
- compatibility with silicon processing planar technology
- reproducible and reliable processing
- low cost & low power consumption

#### **Perfect high-frequency properties:**

high magnetization  $M_S$ low coercive force  $H_C$ high magnetic susceptibility  $\mu$ high electrical resistivity  $\rho$ 

Ion-beam sputtering at variable regimes: substrate T

target composition atmosphere of deposition (Ar,  $N_2$ ,  $O_2$ )













# X-ray diffraction, Cu $K_{\alpha}$ , grazing incidence of 5 degree



#### **Comprehensive characterization**

- Identification of phase composition of granules and matrix
- Reasonable size characterization (estimation of D<sup>coh</sup>)

Phase identification: Rietveld refinement by *FullProf* program

#### Grain size estimation: Scherrer formula

$\Delta(2\theta)_{L} =$	(2)	(180)	λ	
	(1)	(π)	Dcosθ	

*D*<sup>coh</sup> ~ 1-4 nm

Modern approach: Fourier transform of diffraction patterns

B.D.Hall *et al* J. Appl. Crystallography 33 (2000)

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# **Typical magnetic properties of metal-insulator films: random or in-plane orientation of magnetic moment**



# Experimental







## **FeCoZr-CaF<sub>2</sub>: Structure and phase composition**





Phase composition

#### **Origin of growth-induced anisotropy:**

- Surface oxidation of granules
- Effect of matrix composition
- Substrate temperature



# Formation of granular structure in nanocomposite *M-I* films

Criteria:

no chemical compounds

k low solubility
between
components

high difference
 in M and I surface
 energies



## **Factors:**

\* temperature of the substrate

\* energy of
sputtered atoms
or clusters

 concentration of atoms or clusters on the surface

Easy cases

FeCo-Al<sub>2</sub>O<sub>3</sub> FeCo-SiO<sub>2</sub> FeCo-CaF<sub>2</sub>

# Hard case

**FeCo-PbTiO**<sub>3</sub> (*multiferroic film*)

# <u>Way out</u>

Stabilization of granular structure with "core-shell" nanoparticles



Evaluation of magnetization curves: to estimate anisotropy field  $H_a$  and angle  $\alpha$ 

**Difficulties:** (i) *M*(*H*) reflects superposition of *in-plane* and *out-of-plane* anisotropies

(ii) dispersion of easy axis orientations









# **Conclusions on metal-insulator granular films:**

- ✤ Ion-beam sputtering on uncooled substrate allows fabrication of metalinsulator films with non-planar, close to perpendicular magnetic anisotropy with angle α of deviation from the film's normal ≈ 20 degrees
- Perpendicular magnetic anisotropy is associated with the <u>columnar-like</u> <u>shape</u> of agglomerations of metallic nanoparticles
- Magnetic properties of films as a whole are governed with the <u>competition between magnetostatic interaction and shape anisotropy</u> of NPs at high metallic contribution
- Magnetostatic interaction leads to the decrease in shape anisotropy (from ~ 8 to 1.5-2 kOe) and to the increase in angle α against films normal (from ~15° to 35°) in external magnetic field that can be corrected by <u>additional NPs treatment</u> including NPs partial oxidation and films irradiation by heavy ions



#### II. MLs with perpendicular magnetic anisotropy: Co/Pt, Co/Pd, Co/Au, etc.:

high anisotropy constant  $K_{\mu} = 10^8 \, \text{erg/cm}^3$ 

- perpendicular recording media
- perpendicular spin-valve (p-SVs)
- magnetic tunnel junction (p-MTJ) devices



Not only applied point is important: Thin porous films are perfect objects for

- 1) Modelling of magnetization reversal mechanisms;
- 2) Tuning of applied parameters: switching fields, coercive force, ratio between saturation magnetization and remanence

# Magnetic anisotropy origin:

- Interfacial anisotropy:
   Interface electronic effects –
- Interface electronic effects hybridization between Co 3d and Pd 4d at the interface;
- Stress caused by lattice mismatch between Pd and Co.

Roughness, intermixing, alloy formation at the interface play crucial role

# 2) Magnetocrystalline anisotropy:

 $L_{10}$  crystalline structures (Co<sub>3</sub>Pt, Fe<sub>3</sub>Pt)

Chang, J. Alloys Comps 710(5):37-46 · March 2017



## <u>MLs with perpendicular magnetic anisotropy: Co/Pt, Co/Pd, Co/Au, etc.:</u> <u>High-density recording media</u>

#### Ordered arrays of nanodots Recording density is up to 5 Tbit/in<sup>2</sup> (*Hitachi GST, Toshiba u Fujitsu*)



#### Superparamagnetic limit





#### Superparamagnetic limit:

The maximum number of bits per square inch that is commercially feasible on a magnetic storage device (several hundred gigabits per square inch)

#### Superparamagnetic state:

Magnetic moment is oriented along an easy magnetization axis governed with total magnetic anisotropy



Angle between easy axis and magnetization

#### For small nanoparticles energy of anisotropy $K_a V = k_B T$ , and magnetic moment fluctuates

Quasi-paramagnetic behavior of very small magnetically ordered and weakly interacting particles

Observation of SP state is possible when observation time is larger than time of superparamagnetic relaxation



#### <u>MLs with perpendicular magnetic anisotropy: Co/Pt, Co/Pd, Co/Au, etc.:</u> <u>High-density recording media</u>

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Superparamagnetic limit





#### **Continuous films with nanoporous**

structure («antidots»)





# **Porous self-ordered templates for PPM: Morphology requirements**



- Developed morphology of porous metallic films
- Local misalignment of magnetic moments & distorted perpendicular magnetic anisotropy

## Morphology of templates is a crucial issue



# *Co/Pd* films on porous *Al*<sub>2</sub>*O*<sub>3</sub> templates: SQUID-magnetometry

Morphology





The way out: preparation of template with flattened interpore areas by combination of anodization regimes and Ar ion-beam polishing



Fabricated templates: flattened relief at the expense of ordering



# Main objectives research:

- 1. To fabricate flat-surface templates anodized porous matrixes, and prepare porous Co/Pd, Co/Pt ML thin films
- 2. To investigate how the surface relief of Pd/Co/Pd MLs affects magnetic properties of Pd/Co/Pd antidots

## Main task of research:

To fabricate percolated perpendicular media of Pd/Co/Pd MLs with perpendicular magnetic anisotropy, enhanced coercive force  $(H_C > 2000 \text{ Oe})$  and high squareness  $(M_r/M_S \approx 0.8)$ 

# Experimental



#### TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> templates on Ti/Al foil

- Ti or Al foil is cleaned and oxidized in electrolyte (0.3 % of NH<sub>4</sub>F or H<sub>2</sub>SO<sub>4</sub>, respectively)
- Two-stage anodization of Ti (AI) foil in two-electrode electrochemical cell in the combined regime
- Ion-plasma Ar etching during 20 min. is applied for smoothing of templates surface

#### TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> templates on Si wafer

- Ti or Al film of 0.27 or 0.4 μm thickness is deposited by magnetron sputtering on Si wafer
- Ti (Al) film is cleaned, oxidized and anodized (two-stage anodization)
- Ion-plasma Ar etching during 10 min. is applied for smoothing of templates surface

[S.K. Lazarouk et al, Thin Solid Films, 526, (2012)]





# [Co/Pd]<sub>n</sub> multilayers on porous TiO<sub>2</sub> templates (NTs)



# [Co/Pd]<sub>n</sub>/TiO<sub>2</sub>//Si (Ti) Belarusian State University, Minsk, Belarus



# X-ray reflectometry, X-ray diffraction & FT EXAFS oscillations





<i>a</i> <sub>Pd</sub> (Å)	<i>а</i> <sub>СоРd</sub> (Å)				
Continuous MLs					
3.88	3.79				
Porous MLs					
3.87	3.81				

XRR and XRD proves layered structure and CoPd quasi-alloy at the interface



# **Magnetic properties: SQUID-magnetometry & MFM**

 $[Co/Pd]_n/TiO_2//Si(Ti)$ 



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# Mechanisms of magnetization reversal:

### crossover from Kondorsky (in continuous film) to rotational (in porous film)





# **Mechanisms of magnetization reversal:**

 $[Co/Pd]_n/TiO_2//Si(Ti)$ 

#### crossover from *Kondorsky* (in continuous film) to *rotational* (in porous film)





# **Magnetic properties** *vs* **substrate: estimation of** K<sub>eff</sub>

## Co/Pd/TiO<sub>2</sub> // Ti foil

# Co/Pd/TiO<sub>2</sub> // Si wafer



 $[Co/Pd]_n/TiO_2//Si(Ti)$ 





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# In resume: $[Co/Pd]_n/TiO_2$ porous multilayers: Effect of flat-surface template on magnetic properties



## **Conserved perpendicular anisotropy**

- Coercive force  $H_{\rm C} = 2700$  Oe
- Squareness:  $M_r/M_s = 0.7$
- $K_{\rm eff} = 1.9 \cdot 10^6 \, {\rm erg/cm^3}$



# Flat-surface $Al_2O_3$ templates $\rightarrow$ [Co/Pd]<sub>n</sub> porous MLs with smoothed surface

 $[Co/Pd]_n/Al_2O_3//Si$ 



 $[Co/Pd]_n/Al_2O_3//Si$ 





# X-ray photoelectron spectroscopy



#### Ordering in Co/Pd and Co/Pt MLs is not affected by the surface morphology

# **High-resolution XPS**





# **Magnetic properties: fitting with S-W model**

 $[Co/Pd]_n/Al_2O_3//Si$ 



	Coercive field $H_C$ , Oe	M <sub>r</sub> /M <sub>s</sub>	H <sub>K</sub> , Oe
	Continuous ML		
Co/Pd; Co/Pt	1100 – 1200	0.99	
	Porous MLs		
Co/Pd	1900	0.99	2600
Co/Pt	1500	0.99	2000



# Comparison of magnetic properties of porous Co/Pd reflects difference between morphology TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> templates

 $[Co/Pd]_n/Al_2O_3//Si$ 







## Fabrication of FM/AFM porous ML with perpendicular exchange bias: coupling between IrMn (AFM) and Co/Pt (FM) layers



AFM layer to pin the magnetization of FM film in a particular direction by interfacial exchange interaction with an AFM layer

AFM layer – IrMn: resistant to corrosion possess high  $T_N \approx 400$  °C

#### *TiO*<sub>2</sub> *porous template on Si*



#### Si/TiO<sub>2</sub>//IrMn/CoFe/[Pt/Co]<sub>2</sub>

Si/TiO<sub>2</sub>//CoFe/[Pt/Co]<sub>2</sub>/IrMn

Dr. Dmitriy Mitin Experimentalphysik IV Institut für Physik Universität Augsburg





# First magnetometry results: experimental evidence for exchange bias in FM/AFM porous MLs







# First magnetometry results: experimental evidence for exchange bias in FM/AFM porous MLs







### Magnetoresistivity

# Co/Pt//IrMn MLs

non-symmetric MR effect in the film normal direction different types of MR effect in two opposite directions









- ☆ Anodized templates of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with flattened interpore areas favors conservation of perpendicular magnetic anisotropy in porous Co/Pd and Co/Pt thin ML films with smoothed surface relief.
- \* Magnetization reversal in porous films proceeds by rotational mechanism and could be considered within Stoner-Wohlfarth model because of the refinement of magnetic domain structure.
- Further progress in fabrication of porous films for spintronic devices should be focused on porous FM/AFM films with FM layers possessing perpendicular magnetic anisotropy.



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#### MLs fabrication, XRD, AGM

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Thank you for attention!