Thesis statements of PhD work

Modification and study of magnetic thin layers

Merkel Dániel Géza

Eötvös Loránd University Faculty of Science

PhD school of physics

Material science and solid state physics program

Supervisor:

Dr. Bottyán László

Leader of PhD school: Dr. Horváth Zalán

Leader of PhD program: Dr. Lendvai János

MTA KFKI Research Institute for Particle and Nuclear Physics

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INTRODUCTION

One of the main topic in today's research is the sustainable development, which covers all scientific and technical fields. Exploring material properties and applying it for designing more advanced materials and sometimes developing more energy efficient solutions are the matters with material science can contribute to this goal. It is widely prevalent that –since in the region of less than 100 nm the properties of the objects can be significantly different from the bulk one – the nanoscience and nanotechnology can play accentuated role in this process. According to literature, the objects below 100 nm can be classified as 3D nanocrystals, 2D layerstructures, 1D nanowires and 0D nanodots.

The reason why 2D nanolayers exhibit special attributes is the effect of the electron structure variation to the total energy of solid and the increase of the ratio of atoms situated at the interface. The giant magnetic resistance is excelled from the lately discovered nanomagnetic properties (Nobel price 2007), since it has remarkably increased the potential in developing magnetic recording, memory and sensor devices. This revolutionary improvement in the field of designing new materials for recording devices and reading/writing rate of magnetic bits is not over yet. The continuous need for higher storage capacity leads to higher bit density and hence the lowering of the size of individual bits which caused quantum fluctuation in the formerly used inplane magnetized materials. In presently used storage disks, it is general to use bit density over 150 Gbit/inch2 using perpendicular magnetic recording, where the magnetization direction of the magnetic domains point out of the sample plane. For this, new kind of materials with perpendicular magnetic anisotropy (PMA) required. The magnetic anisotropy is the consequence of spin-orbit coupling and so it is related to the symmetry/assymetry of the atomic environment. The origin of asymmetry can arise from the inner properties of atomic lattice (magneticrystalline), the presence of uniaxial mechanical stress (magnetoelastic), or the symmetry breaking effect of the electron shells at the interface. In some special alloys these effects can overwrite the macroscopic anisotropy, and results magnetic easy axis perpendicular to the surface. Such materials are ie. $L1_0$ (face central tetragonal) type CoPt, FePt, FePt, FePd.

For using these materials as magnetic storage media, periodic array of magnetic nanoparticles are needed. Many approaches to the preparation of metal nanoparticles have been reported including chemical reduction, UV photolysis, thermal decomposition, metal-vapor decomposition, electrochemical synthesis and even sonochemical decomposition. The common problems with these methods either the large available particle size, short range of periodicity, high cost or too small preparable area. One possible way to solve these problems can be the production of nanopatterned structures by using silica spheres as mask for ion implantation.

These kinds of scientific researches require expensive infrastructures, where improving performance is crucial. Multilayer mirrors are indispensable devices in slow neutron research. A

Bragg mirror (BM) is a layer sequence of two materials with different neutron optical potential, which can be used as a neutron monochromator. In most applications higher harmonics are to be rejected. As an alternative to filtering, a suitable sinusoidal-like modification of the mirror's bilayer depth profile suppresses higher harmonics.

Supermirrors (SM) (a series of bilayers with increasing period) extend the high reflectivity region without a distinct Bragg reflection. They are widely used in neutron guides and in advanced neutron optical devices. If consisting of alternating ferromagnetic and nonmagnetic layers SMs can be used as neutron polarizers.

AIM OF THE WORK

One of the goals of my doctoral work was to understand the structural and magnetic properties of FePd system, and to study the mixing and diffusion processes after annealing and low energy helium irradiation

I introduce a method which I demonstrated in FePd system, namely creating magnetic nanopattern in a PMA material, where self assembly silica balls were used as an irradiation mask.

The magnetic and structural studies on self ion (Ni^+) irradiated Nickel layers prepared with different methods can be guide for magnetic anisotropic thin film research.

As an application of the latter mentioned fundamental research, I studied two subjects which are very important in the field of Fe/Si magnetic mirror production.

First I studied the possibility of decreasing residual stress with ion irradiation in Fe/Si magnetic supermirrors prepared by sputtering technique and the effect of irradiation to the neutron optical properties of the mirrors.

Second I examined different methods how to neglect higher order harmonics reflection of magnetic Fe/Si Bragg mirrors, hence make it possible to use it as a monochromator and polarizer simultaneously.

Applied techniques

The ^{57}Fe environments presented in FePd samples were identified by conversion electron Mössbauer spectroscopy (CEMS) and the corresponding hyperfine magnetic field, quadrupol splitting and isomer shift was calculated. Synchrotron Mössbauer reflectometry (SMR) was found to be an excellent technique to study the mixing of adjacent layers in atomic scale in isotope periodic multilayers, hence gather information about diffusion processes in the samples. Besides SMR, neutron reflectivity (NR) measurements were used to study diffusion processes and also to study the neutron optical properties of magnetic neutron mirrors.

To determine the anisotropy of coercive force, remanence and magnetic saturation energy magneto-optical Kerr effect (MOKE) was used. The imaging of the magnetic domain structure of the sample was done by magnetic force microscopy (MFM) and the imaging of structural properties of the sample surface was performed by atomic force microscopy (AFM).

The inner structure of samples were experienced by transmission electron microscope (TEM) in diffraction and in imaging mode and by high angle X-ray diffraction (XRD). To determine the inner stress grazing incidence X-ray diffraction was used (GIXRD). I order to produce high quality samples for my experiments molecular beam epitaxy (MBE), electron gun evaporation (EGE) and sputtering preparation techniques were applied.

As a part of my work both in sample preparation and in investigations major development had to be achieved. I realized the shutter and quartz crystal control in MBE instrument, with infinite number of layers could be automatically -without human interaction- prepared with precision of one percent of a monolayer.

I have built MOKE device and developed a controller program for it, which I used during the work of this thesis and also in other projects.

I have major contribution in building and testing GINA polarized neutron reflectometer in Budapest Neutron Centre. The controlling software of the instrument is fully the result of my work. Significant part of neutron reflectometric measurements mentioned in my thesis was done on this instrument.

THESIS STATEMENTS

1. By optimizing the layer thicknesses and the MBE growth parameters I succeeded **to** prepar**e** (~81 **%** $L1_0$) ordered epitaxial FePd films on MgO(001) substrate. Such highly ordered FePd has not been reported yet in the literature (according to the Web of Science) [MD1],[KA].
    a. I found ion irradiation effects in the ^{57}Fe Mössbauer spectra of FePd at such high order parameter values (and low irradiation fluences) at which no effects have been reported by any other method in the literature In accordance with the literature, I was able to distinguish three ^{57}Fe hyperfine field distributions, and assigned them to a planar four-fold and a cubic Fe-site characteristic for the $L1_0$ and the fcc phase and an iron-rich Fe-site of even higher number of nearest neighbors [MD1],[KA]..
    b. By comparing the fluence dependence of the lattice parameters and that of the ^{57}Fe Mössbauer quadrupole splitting I inferred that an out-of-plane compressive and an in-plane tensile stress is present in the FePd films [MD1].

2) From synchrotron Mössbauer reflectomtric (SMR) and neutron reflectometric (NR) results on isotope-periodic ordered and disordered epitaxial MgO(001)/ [^{57}FePd/^{nat}FePd]$_{10}$ films irradiated by 60, 130 és 400 keV He$^+$-ions I concluded [MD2] that the above-mentioned Fe sites possess individual ion-mixing diffusion coefficients, and the variation of the volume fraction of those local environments consequently appears in the variation of the average diffusion coefficient upon irradiation fluence. I determined the fluence dependence of the effective diffusion lengths of these Fe-sites for the applied three He$^+$ irradiation energies and concluded that the effective ion-mixing diffusion is strongly hindered in L1$_0$ environments in the crystallographic *c*-direction. The Fe self-diffusion mainly propagates via the iron-rich and fcc-like environments in the crystallographic *c*-direction.

3) Fit results of SMR and NR curves measured on isotope-periodic, (0,0,1) orientation epitaxial MgO(001)/[^{57}FePd/^{nat}FePd]$_{10}$ multilayer samples heat treated at various temperatures for various retention times enabled me to draw the following conclusions on the individual Fe-sites [MD3]:

   a) The pre-exponential factor and activation energy of diffusion in the crystallographic *c*-direction are: D^0_{L10} =5.76×10^{-14} m^{2}s^{-1} Q_{L10} =1.82 eV, D^0_{fcc} =1.32×10^{-13} m^{2}s^{-1} Q_{fcc} =1.48 eV, D^0_{Fe} =1.01×10^{-13} m^{2}s^{-1}, Q_{Fe} =1.39 eV, respectively.

   b) The volume fraction of the iron-rich Fe-site of highest Fe self-diffusion coefficient does not exceed a few percent in any of the samples, therefore the self-diffusion length is dominated by the fcc site which has a two times lower self-diffusivity. As compared to this latter, the diffusion coefficient is two orders of magnitude lower in the L1$_0$ component in the studied temperature range of 500–800 K, i.e. Fe self-diffusion is strongly hindered in the crystallographic *c*-direction.

4) Comparing the formulae of thermal diffusion and ion-beam mixing, I was able to assign hypothetical heat treatment temperatures of 1400 K and 1000-1500 K to the 130 keV and 400 keV He$^+$-irradiations, respectively, at which an identical amount of thermal diffusion mixing occurs in the same period of time.

5) I explained the constant shift of diffusion length deduced from NR- and SMR-data, respectively, to the footprint difference of the beam in the SMR and NR experiment. The

lateral thickness modulations are averaged for a cm-wide and a 0.2 mm wide footprint in the case of NR and SMR experiments, respectively, leading to a virtually larger diffusion mixing and somewhat diminished Bragg-peak intensity in the NR case as compared to the SMR spectra, where the effect is much smaller. [MD4].

6) As a practical application of the results in 1) and 2) I was able to produce an out-of-plane periodic magnetic dot pattern by an ion-lithographic method, which may have implications in the perpendicular magnetic recording. Applying a monolayer of SiO_2-spheres of an average diameter of 200 nm as an irradiation mask the lateral pattern of the spheres was reproduced in the FePd-layer by 100 keV iron and 35 keV neon irradiation of respective fluence [MD5].

7) I found a strong dependence of own-ion irradiation effects on the preparation method of Ni films (electron beam evaporation – EGE, or molecular beam epitaxy, MBE). Coercivity, residual stress, magnetic anisotropy of the EGE-samples were found far beyond the equilibrium values. Coercivity and residual stress are 300 Oe and 1.41 GPa, and 16 Oe and 0.31 GPa, respectively for the EGE and MBE-prepared films, respectively. In MBE-prepared films the residual stress changes sign upon increasing fluence of irradiation from tensile to compressive. I found a relation between the residual stress and the two-fold and four-fold magnetic anisotropy coefficient. [KZ].

8) Making use of the results 7) I studied the relation between the technologically disadvantageous residual stress and the neutron optical properties in Fe/Si magnetic neutron supermirrors. The originally 1.76 GPa residual stress int he in Fe/Si supermirror could be decreased to a tolerable level by 500 keV He^+-ion irradiation. The price for decreasing the residual stress to the 60 or 80 % of its initial value by irradiation is that the reflectivity of the supermirror at the critical angle decreases by 17 and 24 percent as compared to its as-prepared value, while the polarization efficiency is decreased by 2 to 4 %-kal. [MD6].

9) As a practical application of Result 2) concerning diffusion interface rounding, I was able to prepare polarized neutron mirrors of strongly reduced higher harmonics intensity by engineering the layer's depth profile during growth and by post-preparation ion irradiation. I reduced the total intensity of the higher order Bragg-reflections from 22 % 2.2 % without

considerable loss of the first Bragg-peak intensity. In certain cases I found an increase in the polarization efficiency. The use of aperiodic layer structures in polarized neutron Bragg-mirror design is a rather new approach not found so far in the literature [MD7].

PUBLICATIONS RELATED TO THE RESULT OF THE THESES

[MD1] D. G. Merkel, M. Major, A. Németh, Sz. Sajti, F. Tanczikó, L. Bottyán, Z.E. Horváth, J. Waizinger, S. Stankov, A. Kovács; „Modification of local order in FePd films by low energy He^+ irradiation"; J Appl Phys 104: 013901 (2008)

[KA] A Kovács, D.G. Merkel, F. Tanczikó, S. Stankov, Y. Hirotsu, L. Bottyán; „He+ ion irradiation-induced disordering in $L1_0$-FePd thin films: Ion fluence dependence"; Scripta Mater 58: 635-638 (2008)

[MD2] D. G. Merkel, A. Kovács, F. Tanczikó, Sz. Sajti, M. Major, Cs. Fetzer, R. Rüffer, S. Stankov and L. Bottyán: "Self-Diffusion of Iron in $L1_0$ FePd films Upon He-irradiation"to be published

[MD3] D. G. Merkel, Sz. Sajti, F. Tanczikó, M. Major, Cs. Fetzer, A. Kovács, A. Rühm, J. Major, R. Rüffer and L. Bottyán: "Self-Diffusion of Iron in $L1_0$ FePd film - as revealed by reflectometric methods"to be published

[MD4] DG Merkel, Sz Sajti, Cs Fetzer, J Major, R Rüffer,A Rühm, S Stankov, F Tanczikó, L Bottyán; "Isotope-periodic multilayer method for short self-diffusion paths – a comparative neutron and synchrotron Mössbauer reflectometric study of FePd alloys"; J Phys Conf Ser 211, 012029 (2010)

[MD5] D. G. Merkel, F. Tanczikó, Z. Zolnai, N. Nagy, G. Vértesy, J. Waizinger , L. Bommer and L. Bottyán; "Magnetic patterning perpendicular anisotropy FePd alloy films by masked ion irradiation"; J. Appl. Phys. 109, 124302 (2011)

[KZ] K. Zhang, K. P. Lieb, D.G. Merkel, M. Uhrmacher, N. Pilet, T. Ashworth, and H. J. Hug; "Ion-induced magnetic texturing of Ni films, (Domain structure and strain)"; Nucl Instr Meth B 257,379 (2007)

[MD6] D.G. Merkel, Z.E. Horváth, D.E. Szőcs, R. Kovács-Mezei, G. Gy. Kertész and L. Bottyán;" Stress relaxation in Fe/Si neutron supermirrors by He^+ irradiation"; Physica B, 406, 3238 (2011)

[MD7] D.G. Merkel, B. Nagy, Sz. Sajti, E. Szilágyi, R. Kovács-Mezei and L. Bottyán, „Tayloring neutron optical performance of Fe/Si multilayers" to be published