Mapping Interfaces in Magnetic Thin Films with Neutron Reflectometry

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Abstract

The article discusses the importance of Polarized Neutron Reflectometry (PNR) in understanding magnetic structure of thin films. A PNR has been installed in the guide tube laboratory of Dhruva reactor. This instrument has been used successfully to understand magnetic structure in thin films. Some of the results obtained on magnetic non-magnetic multilayer samples have been presented, to demonstrate how PNR has been successful in characterizing interface magnetic structure.

Introduction

Polarized neutron reflectometry is one of the most important non-destructive tools, in understanding and characterizing interfaces in various thin films of interest. Historically Fermi and Zinn were the first to report in the pages of Physical Review journal in 1946, neutron reflectivity measurement for finding out coherent nuclear scattering cross-section of various materials [1]. Approximately a decade later the first report on x-ray reflectivity for thin film characterization from L. G. Parratt appeared [2]. The reincarnation of neutron reflectometry as a useful tool for studying thin films and interface magnetic structure is due to G. P. Felcher of Argonne National Laboratory in 1980s. Later, his comments in a popular article written in Neutron News is worth mentioning [3]:

“Ten years ago at a modest spallation-neutron source at Argonne National Laboratory, a “gizmo” was installed which was later christened as a reflectometer. The popularity of the gizmo spread like wild fire: now virtually all neutron sources possess at least one of them. Some are graced by splendid names: CRISP and SURF at Rutherford, TOREMA at Jülich, DESIR in Saclay and EVA in Grenoble.”

It is the rich information content with resolution in nanometer length scale regarding physical and magnetic structures of thin films, that has made Polarized Neutron Reflectometry (PNR) such an important and popular tool. The popularity of neutron reflectometry is well augmented by that of X-ray Reflectometry (XRR). Both use the phenomena of reflection of waves from thin film surfaces. Since the x-rays interact with the atomic electron cloud and the neutrons with the nuclei, the refractive index for x-rays depends on the electron density of the material and the refractive index for neutrons depend on the coherent scattering length density for neutron-nuclear interaction in the material. This basic difference makes them complementary techniques for study of surfaces and interfaces in thin films. In addition, the neutron possesses a magnetic moment of -1.91 μN (nuclear magneton) and PNR is ideally suited for understanding magnetic structure of multilayer samples. PNR has gained importance also because of rapidly growing interest in thin film multilayers of magnetic and non-magnetic materials, giving rise to various important effects like Giant Magneto-Resistance and Spin-Valve effects. These are artificial
materials that are important, fundamentally as well as technologically. Spin Valve based DRAM memory devices have already appeared in the market. It is important to characterize these materials at nanometer length scale, to correlate their property-structure relationship. In recent years PNR has come handy in such studies. Another important property of neutrons is its capability to distinguish between the isotopes: hydrogen and deuterium, because the coherent scattering lengths are quite different for these two isotopes. This makes neutron an ideal tool to study liquid air or liquid/liquid interfaces and organic films. Presently neutron reflectometry technique is considered so important, that the Rutherford Appleton Laboratory, U. K. in their recently installed second target station at ISIS spallation neutron source, has installed a so-called neutron reflectometer “village” consisting of three neutron reflectometers: one designed for horizontal sample geometry targeting liquid-air interfaces, one for vertical sample geometry for studying magnetic interfaces and another one for studying off-specular or diffuse reflectivity from surfaces and interfaces.

A Polarized Neutron Reflectometer (PNR) has been built in the Dhruva guide tube laboratory by the Solid State Physics Division, BARC. This reflectometer is being used routinely to study magnetic structure in multilayer and thin films. We will briefly discuss some of the results obtained from this instrument on samples of interest.

**Brief Exposition to Neutron Reflectometry**

A neutron at grazing incidence, experiences an average potential in a medium, arising from neutron–nucleus interaction:

$$V(R) = \frac{2\pi\hbar^2}{m} \rho(R)b_{coh}$$  \hspace{1cm} (1)

Where ‘V(R)’ is the number density of the scattering centres in the medium and ‘b_{coh}(R)’ is the coherent scattering length for each scattering centre. This potential translates to a refractive index ‘n’ for a medium, given by

$$n = 1 - \frac{\lambda^2}{2\pi} \rho b_{coh}$$  \hspace{1cm} (2)

Where ‘\lambda’ is the wavelength of the neutron, This simple expression tells us that depending on the sign of ‘b_{coh}’, the refractive index can be less than or more than 1. For most materials ‘b_{coh}’ is positive and the refractive index is marginally less than 1: \(n = 1-\delta\), where \(\delta\) is typically about \(10^{-5} - 10^{-6}\). Neutrons are totally reflected up to a critical incident angle \(\theta_c\) given by:

$$\theta_c = \lambda \sqrt{\frac{\rho b_{coh}}{\pi}}$$  \hspace{1cm} (3)

For a good reflector like nickel, the value of wavelength dependent critical angle \(\theta_c\) is 6 arc minutes/Å. For a medium in which the scattering centres have magnetic moments, neutrons, because of their inherent magnetic moment, will experience a potential energy in a field ‘B(R)’, other than the nuclear potential, given by:

$$V_{mag}(R) = -\mu N \cdot \vec{B}(R)$$  \hspace{1cm} (4)

If one considers that the film is so magnetized that the magnetic moments are all aligned giving the internal field ‘B(R)’, then the refractive index of the medium for polarized neutrons is given by:

$$V(R) = \frac{2\pi\hbar^2}{m} \rho(R) [b_{coh} \pm b_{mag}]$$  \hspace{1cm} (5)

We have defined a magnetic scattering length ‘b_{mag}’ arising out of ‘V_{mag}’ where, the sign before the magnetic scattering length depends on the neutron magnetic moment parallel (+) or anti-parallel (-) with respect to the polarization of the sample. We will use the term up (+) and down (-) for these two polarizations. Also, now the critical angles for total external reflection for up (+) and down (-) neutrons are different:
This shows that polarized neutron reflectometry from magnetic samples will enable one to map the magnetic field in a magnetic sample. Above the critical angle, once the neutron beam starts penetrating the medium, it gets reflected at every interface due to refractive index contrast and the reflected amplitudes interfere. The measured reflectivity becomes structured. The oscillations in reflectivity profile above the critical angle bear the signature of layered structure of a thin film.

Fig. 1 shows simulated PNR profiles \( R^+ \) and \( R^- \) for a Fe-Cr multilayer thin film for up (+) and down (-) neutrons. The reflectivity profile has been plotted as a function of momentum transfer ‘\( Q \)’

\[
\theta_c^\pm = \frac{\lambda}{\sqrt{\rho \left[ b^\text{coh} \pm b^\text{mag} \right]}}
\]

Fig. 1: Spin-up \( R^+ \) (red line) and spin-down \( R^- \) (blue line) reflectivity profile for an Fe/Cr multilayer thin film consisting of 10 bilayers of Fe and Cr. The Bragg peaks are due to periodicity of the bilayers and the Kiessig oscillations are signature of total thickness of the film. The critical angle for \( R^- \) is lower than \( R^+ \) because refractive index for ‘\( + \)’ and ‘\( - \)’ neutrons are different.

The Fe-Cr film consists of ten periodic bilayers of Fe-Cr with each bilayer approximately 10 nanometer (nm) thick: total thickness being 100 nm. The difference in the critical angles between \( R^+ \) and \( R^- \) is due to the difference in potential seen by ‘\( + \)’ and ‘\( - \)’ neutrons. The periodic repetition of the bilayer gives rise to so-called “Bragg peaks” in the reflected intensity, similar to the diffraction peaks arising from atomic periodicity in crystal lattices. The oscillations in intensity between two Bragg peaks are due to the interference of neutron waves, reflected from the top and bottom the film. These are called “Kiessig oscillations” and are signatures of total thickness of the film. The Bragg peaks are absent in \( R^- \) due to the fact, that for the down neutrons there is a loss of contrast between Fe and Cr layers (negative sign in potential, eqn. (5)) and the periodic structure of the film is lost. This example brings home the point, that the profiles \( R^+ \) and \( R^- \) bear the signatures of physical and magnetic structure of the Fe-Cr thin film.
Polarized Neutron Reflectometer in Dhruva

The PNR instrument in Dhruva had been installed on a curved neutron guide in Dhruva. Neutron guide tubes transport neutrons using the phenomenon of total external reflection from guide walls. The present guide tubes at Dhruva, glass coated with Ni, were fabricated and installed by the Solid State Physics Division, to take neutron beams out from the reactor hall to guide tube laboratory. Fig. 3(A) shows a photograph of the reflectometer and schematic of the same is shown in Fig. 3 (B) [4]. The reflectometer has been designed for vertical sample geometry and it can be used for specular as well as off-specular (or diffuse) reflectometry (when angle of incidence is not equal to angle of reflection). The neutron beam coming from Dhruva reactor through the curved guide is reflected by [113] planes of a Si monochromator, to select a monochromatic beam of 2.5 Å neutrons [neutron beams shown by red arrows in Fig. 3 (A)]. These neutrons are collimated to few arc minutes using a collimator made from Cd slits. The collimated and monochromatic beam of neutrons can be polarized using a polarizing super mirror made from Co-Fe/Ti-Zr layers. This monochromatic, highly-collimated and polarized beam of neutrons is reflected from a vertical sample, magnetized using a permanent magnet of 2K Gauss strength and located at the centre of a rotation stage. With the sample fixed at the centre, the sample stage is rotated in steps (typically about 1 arc minute) to collect the reflectivity pattern of the sample as a function of angle of incidence (θ). Fig. 3 shows the scattering geometry. In specular reflectivity, angle of incidence (θ) and angle of reflection (θ) are equal. Since we use a PSD in this instrument, we have the liberty to collect off-specular reflectivity data also on this instrument (θ ≠ θ). Off-specular reflectivity can reveal surface and interface morphology. Presently we will discuss results of specular reflectometry only.

Fig. 3: (A) Photograph of the polarized neutron reflectometer at Dhruva and (B) schematic of the same. ‘M’ is the monochromator, S1’ S2’ S3’ are the cadmium slits for collimator, ‘SM’ is the super mirror polarizer, Sa’ is the sample stage with magnet, ‘An’ is the analyzer super mirror and ‘PSD’ is the 3He position sensitive neutron detector.
The rotation stage can rotate with a precision of about 20 arc seconds and is capable of carrying a load up to 400 Kg. It had been designed and fabricated in the Centre for Design and Manufacture, BARC specifically for the reflectometer. The reflected beam is detected by a 30 cm long He\(^3\) neutron Position Sensitive Detector (PSD), fabricated in the solid state physics division. The PSD has a position resolution of approximately 2 mm. The D. C. flipper in the beam is used to flip the direction of neutron spins for measuring reflectivity for spin-up (+) and spin-down (-) neutrons. Due to intensity constraints we do not use a spin analyzer for the reflected beam at present, though the analyzer is available. In the present set up, we are able to determine physical and magnetic moment density as a function of depth in the sample.

Some of the results are discussed here to demonstrate the importance of polarized neutron reflectometry in pinning interface structure of thin films.

**Data Collection and Analysis**

A stepper motor-based control system has been designed for the high precision translation and rotation stages. The monochromator is mounted on a tilt and rotation stage assembly. The spectrometer table can rotate around the monochromator to facilitate \(\theta - 2\theta\) coupling between the monochromator and the table. This allows changing the incident wavelength, if required. The collimator is mounted on a high precision linear stage, which can move the collimator in steps of 10 microns across the beam. The sample and the magnet are mounted on a linear stage with one-micron step size on top of the rotation stage. Sample surface is brought to the centre of the rotation stage with the help of this linear stage. The control system for all the stepper motors is an integral unit with the drivers and the power supplies located in it. It is operated from the instrument’s PC through RS232 serial port communication.

Typical reflectivity data collected at a certain angle of incidence \(\theta\) looks like a Gaussian on the He\(^3\) PSD channels [insets, Fig. 4]. The integrated counts under the peaks, after background subtraction, give intensity at particular angles as shown in Fig. 4.

![Fig. 4: A typical neutron reflectivity profile as a function of angle, collected on the PNR at Dhruva. The insets show intensity as a function of channel no. for a specific angle of incidence. Integrated intensity under each peak after background subtraction gives one data point in the reflectivity profile.](image)

The analysis of PNR data requires getting the structure of thin film sample in terms of layer thickness, magnetic moment density, interface composition and interface roughness from the experimental data in \(Q\) space. Ideally, it is through a Fourier inversion from momentum space \((Q)\) one can get the structure (magnetic or physical) in real space \((R)\). In reality we can collect data only over a limited momentum \(Q\) or angular range and direct Fourier transformation is not possible. We take recourse to a ‘model-fitting’ where we start with an assumed structure of the thin film sample and generate a reflectivity pattern corresponding to this structure. The initial model is modified through a \(\chi^2\) minimization program, using some error minimization software to modify the physical parameters, so that we generate an intensity profile matching the experimental data. We have developed an optimization software using ‘Genetic Algorithm’.
Samples Studied

a. Ni/Ti multilayer

Thin film multilayers of Ni/Ti have found useful applications in the field of soft x-ray and neutron optics, where they are used as highly reflecting mirrors, supermirrors, polarizers and monochromators etc. Further, TiNi alloy prepared in thin film form, shows interesting shape memory effect and this has been utilized to develop different Micro-Electro Mechanical Systems (MEMS) such as cantilevers, actuators etc. Bulk Ni/Ti alloys are also important technological materials. We had prepared Ni/Ti multilayers of various modulation lengths on glass substrate by vacuum deposition. The sample discussed here had ten Ni/Ti bilayers [Ni 5 nm and Ti 7 nm] on glass substrate. The aim of the study was to understand the growth of alloys at the interfaces as a function of annealing (5). The samples were annealed first at 300 °C and then at 400 °C for a fixed time of 1.5 h. PNR was carried out on all the samples before and after annealing. Fig. 5 shows the PNR data from the sample before and after annealing. The solid red circles are data for $R^+$ and the open blue circles are for $R^-$. Solid lines are fits to the data. The drop in the intensity of the Bragg peak and the gradual merging of the profiles for $R^+$ and $R^-$ are due to mixing of Ni and Ti at the interfaces.

We had also carried out XRR on the same sample (data not shown). Analyzing the XRR and PNR data, we derived the physical and magnetic structure of the sample. To highlight the complementary role of XRR and PNR, we show the plots of physical density as obtained from XRR from the sample before and after annealing at 300 °C and 400 °C together with the corresponding magnetic moment density profiles in Figs. 6 (i) and 6 (ii) respectively. The physical density of the as-deposited sample shows clear step-like oscillations of density as a function of depth (6(i) (a)) signifying periodic Ni and Ti layers of nearly bulk density. The corresponding magnetic moment density, obtained from PNR also shows the same step-like nature as a function of depth. Ni is the magnetic component in this sample and we found an average magnetic moment of 0.4 $\mu_B$ (Bohr magneton) per Ni atom in the Ni layers and a zero magnetic moment density for the Ti layer from PNR data. As we annealed the sample, alloying occurred at the interfaces. Figs. 6(ii)(b-c) clearly show progress of alloying at the interfaces as snap-shot pictures of density profiles obtained from XRR. We determined the composition of the alloy layers at two interfaces, which showed small asymmetry for Ni on Ti with respect to Ti on Ni. This trend is also reflected in the magnetic moment density profile. The magnetic moment density profiles have been obtained from PNR data. As the alloying progressed at the interfaces, the magnetic layers got thinner as seen in Figs. 6(ii)(b-c). Only the Ni layers remained

![Fig. 5: $R^+$ (red solid circles) and $R^-$ (blue open circles) reflectivity profile from Ni/Ti multilayer sample along with the fits (black lines) for (a) as-deposited, (b) annealed at 300 °C and (c) annealed at 400 °C](image-url)
magnetic, the interface alloy layers and the Ti layers had zero magnetic moment density. Also the average magnetic moment per Ni atom reduced to 0.1 $\mu_B$ due to loss of neighbors for Ni atoms at the interfaces. This study allowed us to quantify the nature of alloying at Ni/Ti interfaces in this sample, physically and magnetically, with a spatial resolution of few nanometers! Such resolution is barely possible with any other technique.

**Fe-Au multilayers**

A number of studies have been done in recent years in ferromagnetic/non-magnetic multilayer thin films with an aim to find the effect of interface structure on magneto-resistance. We have carried out a series of studies on Fe-Au multilayer samples [6]. We varied the Fe layer thickness systematically and obtained the interface structure in each case through PNR and XRR. Our aim was to correlate the magneto-resistance in these samples, with their physical and magnetic structure at the interfaces. Presently we discuss only the PNR data at Dhruva and the details of magnetic moment at the interfaces.

We obtained PNR data from 3 samples of nominal structure: Si Substrate/[Fe($t_Fe$ nm)/Au(5 nm)]$_{10}$, with $t_Fe$ = 3, 5 and 10 nm, respectively, indicating that the Fe layer thickness varied from 3 nm to 10 nm in these samples. The PNR data from 3 multilayer samples consisting of 10 bilayers of Fe/Au, as described above are shown in Fig. 7, (i)-(iii). The thickness of the Fe layer in each bilayer has been 3 nm, 5 nm and 10 nm in the three samples. For each sample we collected data for spin up (red solid circles) and spin down (open blue circles). The solid lines are the fits to the data. The “Bragg peaks” and “Kiessig oscillations” are clear in the data.

We could ‘map’ the details of the magnetic moment density at the interfaces in these samples from fits to the PNR data. Magnetic Scattering Length Density (SLD) at the interfaces of Fe/Au layers for all three samples with varying Fe layer thickness as obtained from PNR are shown in Fig. 8. It shows two interfaces of an Au layer, Au on Fe (Au/Fe) and Fe on Au (Fe/Au). Vertical dashed lines are the imaginary ideal interfaces. The gradual change in magnetic moment density across interface indicates...
alloying between Fe and Au at the interfaces. The magnetic SLD reaches an average value in the Fe layer and becomes zero in the Au layer. It is also clear that there is a marked asymmetry in the magnetic SLD profile between Fe on Au and Au on Fe interfaces. This happened due to the difference in inter-diffusion of the two species Fe and Au during sputtering. Also for thicker Fe layer the SLD is higher. For Fe layer of 10 nm thickness, the magnetic moment corresponds to $2.18 \mu_B$ (Bohr magneton) per Fe atom, close to the value known for bulk iron ($2.2 \mu_B$). The multilayer with 10 nm thick Fe layer also showed larger change in magneto-resistance with respect to magnetic field compared to other samples. The present study shows that the magneto-resistance of a multilayer thin film is intimately related to its microscopic structure at the interfaces.

Fig. 7: $R^+$ (red circles) and $R^-$ (blue circles) for Fe/Au multilayers with varying Fe thickness from 3 nanometer to 10 nanometer (a-c) with Au layer thickness fixed at 3 nanometer. Solid lines are fits to the data.

Fig. 8: Magnetic scattering length density (SLD) profile at the two interfaces of an Au layer in Fe/Au multilayer, from the fits to PNR data. The two interfaces are Fe on Au (Fe/Au) and Au on Fe (Au/Fe). The vertical dashed lines are imaginary, ideal interfaces.
Conclusions

We have discussed the importance of neutron reflectometry in understanding interface structures in magnetic multilayer thin films. A PNR has been designed and installed in Dhruva reactor guide hall, for characterizing such samples of interest. From data collected on this reflectometer on Ni/Ti and Fe/Au multilayers, we have shown how detailed characterization of interface structure is possible with nanometer resolution. These examples demonstrate that PNR as a characterization tool is extremely important for development of thin film based magnetic devices.

Acknowledgements

The high precision rotation stage for the above reflectometer was designed and fabricated at the Centre for Design and Manufacture, BARC. The data collection software was developed at the Electronics Division, BARC.

References