Structural Characterization of Giant Magnetoresistance Multilayers with New Grazing Incidence X-ray Fluorescence

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We have developed a grazing incidence x-ray fluorescence (GIXRF) technique based on wavelength dispersive (WD) fluorescence equipment with high-brilliance synchrotron radiation x-rays at SPring-8. The technique has been successfully applied to the evaluation of the stratified structure of giant magnetoresistance (GMR) multilayers. Because of the good energy resolution and high count rate of the WD detector, high-quality data about the dependence of fluorescence intensities on the incident angle for the composition elements were obtained. An analysis program based on matrix formalism has been developed, and a good agreement between data and model calculations has been obtained. The results indicate that excessive thermal treatment causes a roughening of inter-layer interfaces, which degrades the magnetic properties of a GMR head.

1. Introduction

In recent years, much activity has been devoted to the development of giant magnetoresistance (GMR) multilayers for use in MR heads for magnetic recording. To meet requests for higher performance, the structure of spin valve GMR heads has been made more complex with thinner layers that enable more than a yearly doubling in recording density. The magnetic properties of these GMR heads are strongly influenced by certain aspects of their structure, for example, the thickness of each layer and the flatness at the inter-layer interfaces.

Ultra-thin multilayer structures of more than 10 stacks are hard to investigate, because even TEM (Transmission Electron Microscopy) imaging shows no clear contrast at the spin valve part (**Figure 1**). X-ray reflectometry, on the other hand, can be used to determine the film thickness, film density, interfacial roughness, and the existence of a mixing layer.

However, because x-ray reflectometry evaluates the layer profile by measuring the refractive index of the layer, spin-valve parts consisting of CoFeB, Cu, and NiFe are hard to distinguish. This is because these materials have similar atomic numbers and densities and therefore have similar refractive indices. In addition, x-ray reflectometry cannot provide direct information on the profile of a composition element, for example,
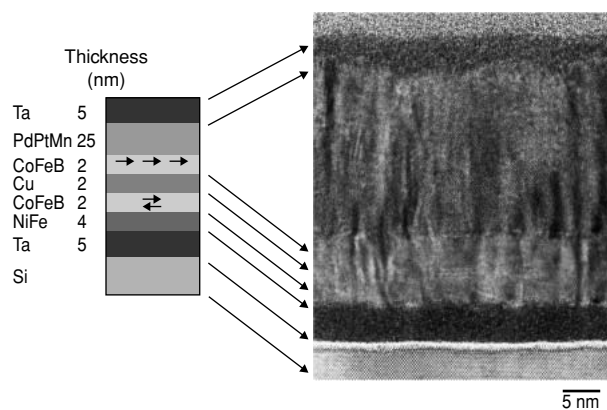

Figure 1
GMR sample structure and its TEM image. The spin valve part (CoFeB/Cu/CoFeB) is hard to resolve.

the interface diffusion of a specific atom. To solve these problems, we developed a grazing incidence x-ray fluorescence (GIXRF) technique using wavelength dispersive (WD) equipment.

2. Experimental setup

X-ray fluorescence measurement provides superior element selectivity than reflectivity measurement, which provides only weak and indirect information about a sample's chemical composition. In x-ray fluorescence, as the grazing angle of the x-ray radiation is varied, the interference effects within the sample change according to the depth profile of the element being investigated. These changes alter the depth profile of the x-ray standing waves in the sample and consequently change the fluorescence intensity, because they alter the flow of x-ray energy. Therefore, by measuring the change in fluorescence intensity as a function of the grazing angle, the depth profile of each element in a complex material system can be determined.

Figure 2 shows a schematic drawing of the measurement configuration. GIXRF has been proposed for several years as a way to evaluate composition profiles,[1)-4)] but it has not been applied to the evaluation of real samples. This is due to complexities in the data analysis and the poor quality of the fluorescence data obtained from the

energy-dispersive SSD (Solid State Detector), which has a maximum count rate of less than 10 kcps and a poor energy resolution. We overcame these difficulties by using a WD detector with a high count rate and good energy resolution and by incorporating the reflectivity data into the estimation of x-ray field intensities in the analysis. The x-ray fluorescence equipment was constructed at undulator beamline BL16XU of the SPring-8 synchrotron radiation facilities by a consortium of 13 industrial companies, including Fujitsu Laboratories.[5)]

Figure 3 shows a photograph of the equipment. For fast commissioning and high reliability, we installed the state-of-the-art WD spectrometer used in the Rigaku RIX3100. We also incorporated a four-axis sample stage used in the Rigaku TXRF300. For high-efficiency detection of fluorescence signals, the WD spectrometer is located directly above the sample. The parallel-optics spectrometer consists of a combination of soller slits and planer analyzing crystals in addition to either an NaI scintillation counter or a flow-type proportional counter. During measurement, the distance between the sample and the
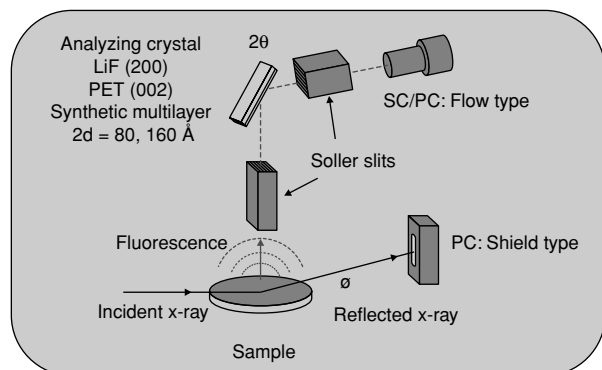

Figure 2
Schematic drawing of grazing incidence x-ray fluorescence configuration. Fluorescence emission from the sample is detected by the wavelength dispersive spectrometer using parallel optics.
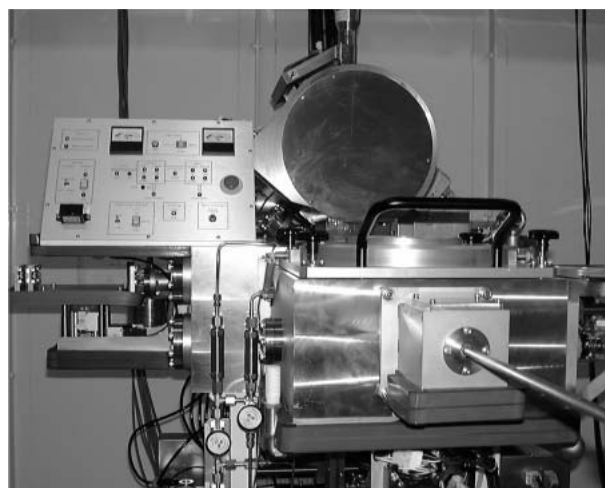

Figure 3
Wavelength dispersive x-ray fluorescence equipment constructed at SPring-8 synchrotron radiation facility by 13 industrial companies including Fujitsu Laboratories. This equipment can measure silicon wafers of up to 12 inches.

detector is 40 cm. A thin (0.6 μm) organic membrane separates the measurement chamber from the WD spectrometer to prevent contamination by dust particles from the spectrometer. To detect elements in the range of B to U, four types of analyzing crystals—LiF(200), PET(002), and two synthetic multilayer analyzers with 2d values of 80 Å (Å = 0.1 nm) and 160 Å—have been prepared.

In addition to the measurement using the WD spectrometer, one side port and one upstream port are provided in the measurement chamber for setting the SSD during the energy dispersive (ED) measurement. The sample stage can hold a wafer of up to 300 mm. The XY position of the stage can be set without changing the sample orientation by using a rotating robot arm that suppresses contamination by dust particles. The grazing angle ø, sample rotation ø, and sample height Z can also be specified. Samples are transferred from the load-locked chamber and placed horizontally on the sample stage in the measurement chamber. By choosing an appropriate sample holder, samples can be placed vertically or obliquely, which enables conventional XRF measurement.

To control the equipment, we developed new software based on LabVIEW. The software controls sample transport, sample alignment, WD measurement, ED measurement, and reflectivity measurement.

3. Experiments

In the experiments, two spin-valve samples with a stratified structure of Ta(6)/PdPtMn(25)/CoFeB(2)/Cu(3)/CoFeB(2)/NiFe(4)/Ta(5)/Si (numbers in parenthesis indicate thickness in nm) that had been fabricated with and without post-thermal annealing at an excessive temperature of 390°C for 3 hours were prepared. These samples were measured at the SPring-8 synchrotron radiation facility. The x-rays from the undulator were monochromatized to 16 keV. A downstream Rh-coated focusing mirror suppressed the higher harmonics, reducing background fluorescence signals from the samples.
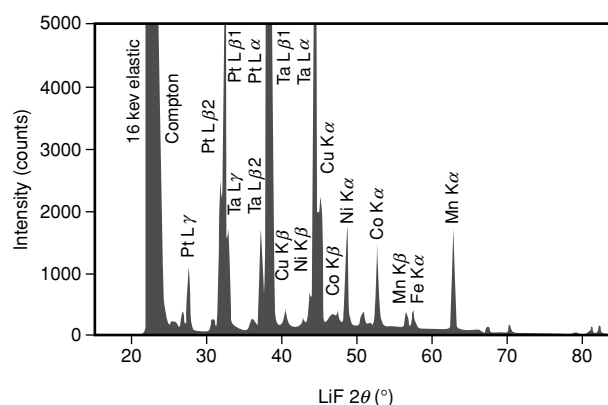

Figure 4
Fluorescence spectrum of GMR multilayer at grazing angle of 1.5 degrees.

In addition, the good energy resolution of the WD spectrometer resolved many fluorescent peaks from the elements in the sample, as shown in **Figure 4**. These features could not be attained by ED measurement using a solid state detector or by conventional WD equipment using continuous x-rays in the laboratory.

In the angle-resolved measurements, a non-overlapping peak of x-ray fluorescence was chosen for each element and the Bragg angle of the analyzing crystal was set at these peaks. The results at grazing angles up to 0.7 degrees for five elements in a sample without post annealing are shown in **Figure 5**. The reflectivity was also recorded (**Figure 6**). The fluorescence intensity shows a clear oscillation structure that originates from the x-ray standing waves generated by interference inside the layers.

4. Data analysis and results

In order to calculate x-ray fluorescence intensities, the intensity of the electromagnetic field in the material has to be known. We extended the reflectivity program based on the matrix formalism of Vidal & Vincent[6] to the GIXRF program, which can also calculate the fluorescence intensities and optimize data by using a layered model. The dissipated energy at each depth is calculated from the electromagnetic field intensi-

ty obtained from the model. The fluorescence intensity is proportional to the dissipated energy. The initial estimate for the electromagnetic field intensity has been obtained from the reflectivity data. Starting from the initial parameters, the fluorescence profiles of each element and the reflectivity profiles are simultaneously optimized in the layered model. **Figure 7** shows the analysis procedure. In this analysis, spin valve parts having different elements at similar densities are resolved from the constraints on fluorescence intensity for the elements that have different depth profiles. These analyses reproduce the complex fluorescence profile very well, as indicated by the solid lines in Figures 5 and 6. The resultant profiles of each element in these two samples are shown in **Figure 8**.

These results indicate that the excessive annealing caused roughness in the interfaces, especially the upper and lower interfaces of the PdPtMn layer. This roughness may have been the result of grain growth in the PdPtMn crystal and may have caused the post-annealing degradation in magnetic properties that was observed. Especially, roughness in the spin valve/ PdPtMn interface would cause degradation, because it would damage the spin valve structure.
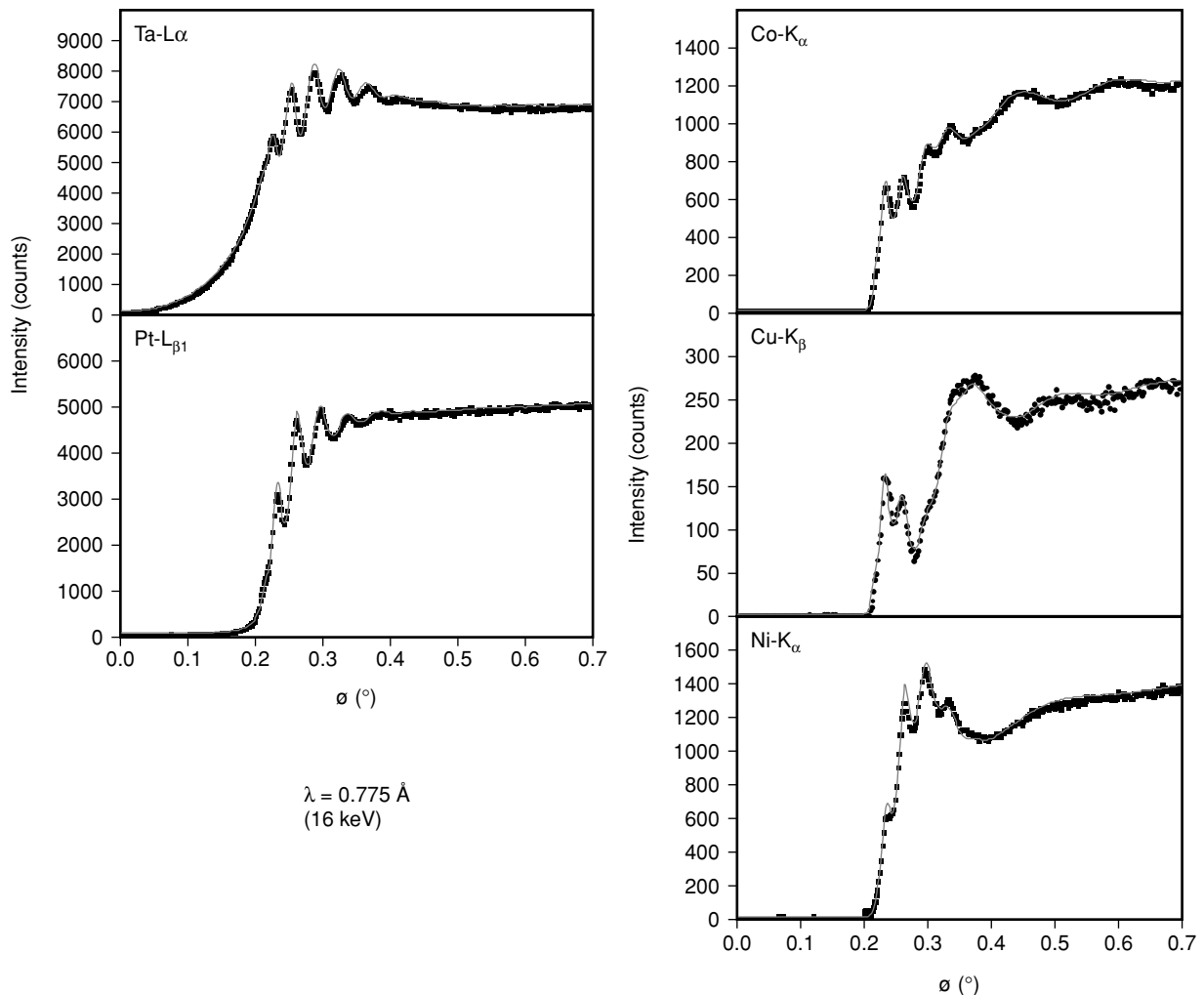

Figure 5
X-ray grazing angle dependence of fluorescence yields for five elements. The solid lines show calculations based on the layered model.

5. Conclusion

A new WD-GIXRF method has been developed in which the atomic profiles of samples can be estimated and applied successfully to evaluate thermal effects in complex GMR spin-valve structures. The broadening of the interfacial width in ultra-thin stratified structures was de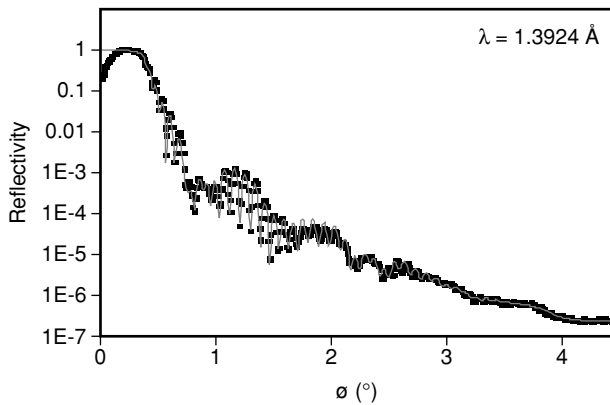termined with an accuracy at the angstrom level. This technique can be applied to wide areas of samples with very thin layers or very low concentrations of elements for the purpose of evaluating their depth profiles and the diffusions of elements.
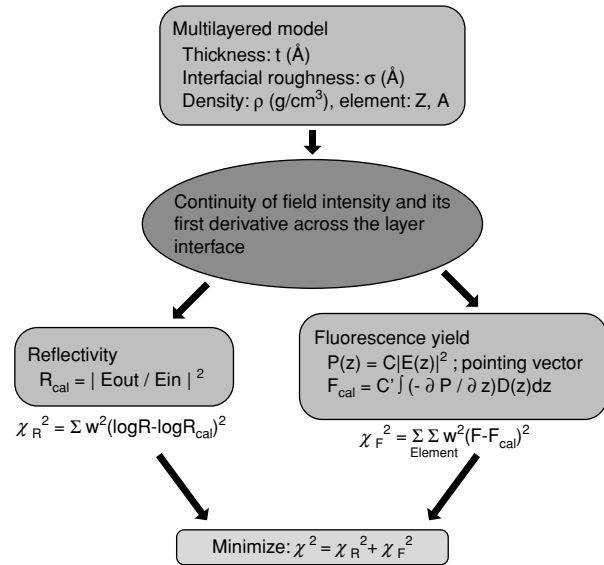

Figure 6
Reflectivity profile of GMR sample. The solid line shows a calculation optimized with the fluorescence yield.

Figure 7
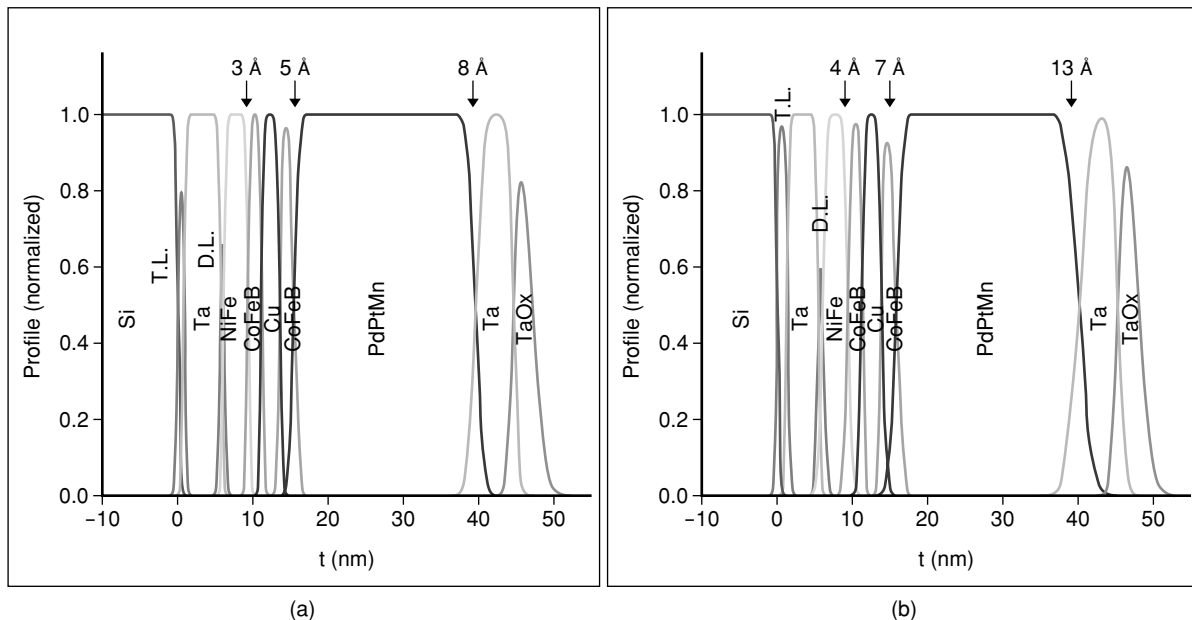GIXRF data analysis procedure.

(a)

(b)

Figure 8
Layer profile of sample before thermal annealing (a) and after annealing at 390°C for 3 hours (b) reconstructed from results of GIXRF analysis. Interfacial roughness at PdPtMn/Ta and PdPtMn/CoFeB was increased by annealing.

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