

Studies on spintronics-related thin films using synchrotron-radiation-based Mössbauer spectroscopy

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Abstract Applications of synchrotron-radiation-based Mössbauer spectroscopy in the “energy domain” to the studies on magnetism of thin films are introduced on the basis of the experiments recently performed at SPring-8, Japan. The measured samples are spintronics-related thin films, such as Co_2MnSn films, layered Fe/Cr films, layered Fe/ Fe_3O_4 films, and Fe_4N films. The validity of the energy domain measurements is demonstrated in the light of industrial applications of magnetic thin films.

Keywords Mössbauer spectroscopy · Synchrotron radiation · Thin films · Layered structures · Interfaces · Magnetism · Spintronics

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1 Introduction

Mössbauer spectroscopy, which can detect local electronic states around nuclei, has been used to study the magnetism of thin films, including that of surfaces and interfaces, in these decades [1]. The role of this experimental method becomes larger in phase with the recent development of “spintronics”, where spins of electrons are actively used for electronic devices.

When Mössbauer spectroscopy is applied to thin films or nanostructures prepared on thick substrates, conversion electron Mössbauer spectroscopy (CEMS) with a radioactive source is usually used in laboratories. With this method, however, it is relatively difficult to perform measurements under special sample conditions, such as at very low temperatures and in magnetic fields. Besides, more and more sensitivity has been required for very thin films and patterned nanostructures prepared on substrates. Synchrotron-radiation-based Mössbauer spectroscopy is a promising method to overcome these problems and makes Mössbauer spectroscopy more attractive for researchers in industrial applications of magnetic thin films and nanostructures.

When the synchrotron radiation, which is basically a “white” light source, is used for Mössbauer spectroscopy, special ideas and setups are required. The method which has mainly been used so far for thin film experiments is “time domain” measurements, where interference patterns of pulsed X-rays resonantly scattered by nuclei are detected as a function of time [2]. By analyzing the time spectra, the size and direction of magnetic hyperfine field can be obtained. This method is quite time-effective and the validity for the determination of the direction of magnetization in thin film systems has been well-demonstrated so far [3, 4]. However, magnetic materials for industrial use often have inhomogeneity in the nuclear environments, which makes the analysis of time spectra complicated. This situation is well-described in Ref. [5]. Therefore, “energy domain” measurements, where spectra are recorded as a function of energy (or the Doppler velocity) as in the conventional Mössbauer spectroscopy, are more desirable for industrial applications.

In this article, examples of synchrotron-radiation-based Mössbauer spectroscopy in the energy domain on thin films performed by our research group are introduced. The validity of the energy domain measurements is demonstrated in the light of industrial applications of magnetic thin films.

2 Experimental

Four kinds of spintronics-related film samples were prepared by vapor deposition or sputtering techniques and synchrotron-radiation-based Mössbauer spectroscopic measurements were performed at SPring-8 in Japan. The samples were (i) Co_2MnSn Heusler alloy films, where high conduction-electron spin-polarization is expected [6], (ii) layered Fe/Cr films, where giant magnetoresistance was first discovered [7, 8], (iii) layered Fe/ Fe_3O_4 films, where strong antiparallel magnetic coupling was discovered recently [9, 10], and (iv) Fe_4N films, where large negative anisotropic magnetoresistance was found recently [11]. The first series of samples (Co_2MnSn) were ^{119}Sn -enriched ($\sim 95\%$) ultra-thin films for the study of magnetic stability, the second (Fe/Cr) and the third (Fe/ Fe_3O_4) were with ^{57}Fe -enriched ($\sim 95\%$) interfacial atomic layers for the investigation of interface structures and magnetism,

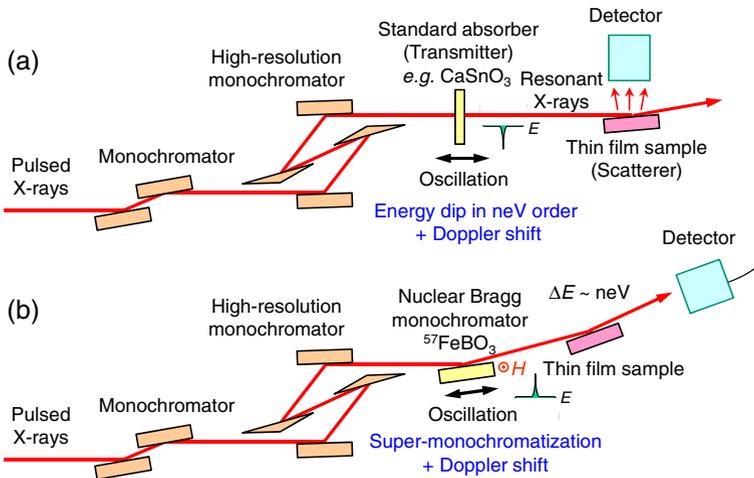


Fig. 1 Typical setups for synchrotron-radiation-based Mössbauer spectroscopy in energy domain for the investigations on thin-film magnetism

and the last samples (Fe_4N) were non-enriched thick films for the measurements under magnetic field at low temperature. All the samples were grown epitaxially on $\text{MgO}(001)$ substrates. The details of the sample preparation methods are described elsewhere, but we note here that the Co_2MnSn layers were prepared by atomically controlled alternate deposition at Nagoya Institute of Technology [6], the Fe_3O_4 layers were grown by reactive vapor deposition in O_2 gas at University of Tsukuba [9, 10], and the Fe_4N films were grown by reactive sputtering in N_2 gas at Tohoku University [11]. Note also here that they are all old materials, with a lot of Mössbauer spectroscopic studies, but renewed views are necessary as materials for spintronics.

As synchrotron-radiation-based Mössbauer spectroscopy in the energy domain, two methods have been developed and optimized for experiments on magnetic thin films. One method is to use a standard nonmagnetic absorber to create a single-line dip with the bandwidth of several neV in the spectrum of the light source [12] (Fig. 1a). The other is to use a nuclear Bragg monochromator to monochromatize the radiation with neV bandwidth [13–19] (Fig. 1b). The dip energy (in the former case) or the peak energy (in the latter case) is modulated by the Doppler shift, accompanied by the oscillation of the standard single-line absorber (in the former case) or the nuclear Bragg monochromator (in the latter case), or alternatively of the samples (in both cases). The X-rays resonantly scattered by the sample are detected, synchronized with the Doppler velocity, to obtain Mössbauer spectra in the energy domain. The experiments with the former setup were performed at the beam line BL09XU of SPring-8 and those with the latter at BL11XU. For the measurements of thin films prepared on thick substrates, a grazing angle geometry is required as shown in Fig. 1, in order to get sufficient number of probe nuclei in the narrow beam path of the synchrotron radiation, which makes the experiments a little complicated in comparison with those for powder or single crystal samples.

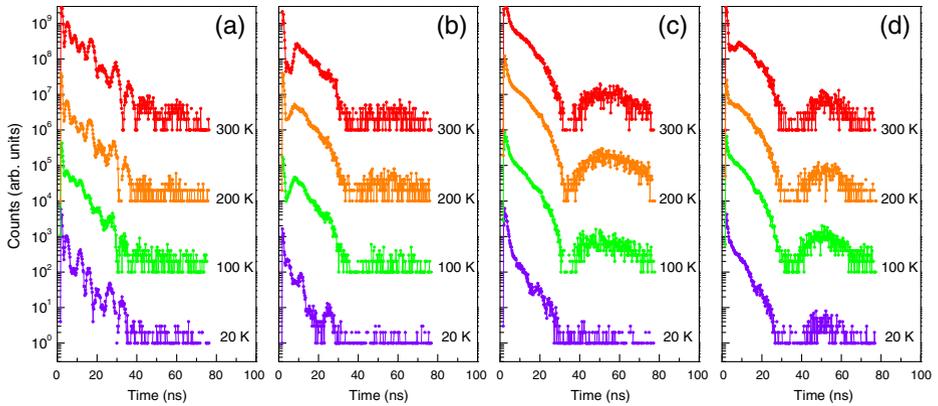


Fig. 2 Nuclear-resonant time spectra for ultra-thin Co_2MnSn films. The samples were designed nominally as atomic stacks of **a** $\text{Co/MnSn/Co/MnSn/Co}$, **b** $\text{MnSn/Co/MnSn/Co/MnSn}$ **c** Co/MnSn/Co , and **d** MnSn/Co/MnSn , and the unit of each Co_2MnSn alloy was multilayered with 6 atomic layers of Cr in each sample (See Fig. 3 for the sample **c**)

3 Results and discussion

The magnetic stability of Heusler alloys films, which are promising candidates for material with highly spin-polarized conduction electrons, is one of the important issues in the field of spintronics. Figure 2 shows ^{119}Sn nuclear-resonant time spectra for ultra-thin epitaxial Co_2MnSn Heusler alloy films with four different thicknesses as a function of temperature. When a Co_2MnSn film is grown epitaxially in the cubic [001] direction with the ideally ordered structure, the film should be composed of alternate stacks of an atomic layer of Co and that of MnSn. Here, the ultra-thin samples were designed nominally as atomic stacks of (a) $\text{Co/MnSn/Co/MnSn/Co}$, (b) $\text{MnSn/Co/MnSn/Co/MnSn}$ (c) Co/MnSn/Co , and (d) MnSn/Co/MnSn , and the unit of each Co_2MnSn alloy were multilayered with 6 atomic layers of Cr in each sample to make the total amount of ^{119}Sn equivalent to 6 atomic layers (See Fig. 3 for the sample (c)), in order to obtain sufficient nuclear resonant signals. An oscillatory quantum beat pattern was observed for the sample with the thickest Co_2MnSn unit as in Fig. 2a, but the pattern becomes unclear as the thickness of the Co_2MnSn unit becomes smaller (and also as the temperature increases). This result suggests that the magnetic hyperfine field, hence the magnetization, decreases as the Co_2MnSn layer becomes thinner. This method in the time domain is quite time-effective with the measurement time typically 3 h per each spectrum. It was, however, not easy to analyze these time spectra with a simple model, which suggests that the magnetic hyperfine fields at the Sn sites are widely distributed. On the other hand, Fig. 3 shows the energy spectra measured using the method shown in Fig. 1a, for the sample composed of the Co/MnSn/Co unit, which is the same as that in Fig. 2c. The concept of this experimental method is described in Ref. [12], and in the present experiment, the energy spectra of the film sample, which was set as a scatterer, was measured using a standard single-line CaSnO_3 absorber, which was set as a transmitter. In the energy spectra, line broadening due to the distribution of magnetic hyperfine fields and its temperature evolution are intuitively seen, although about 10 times

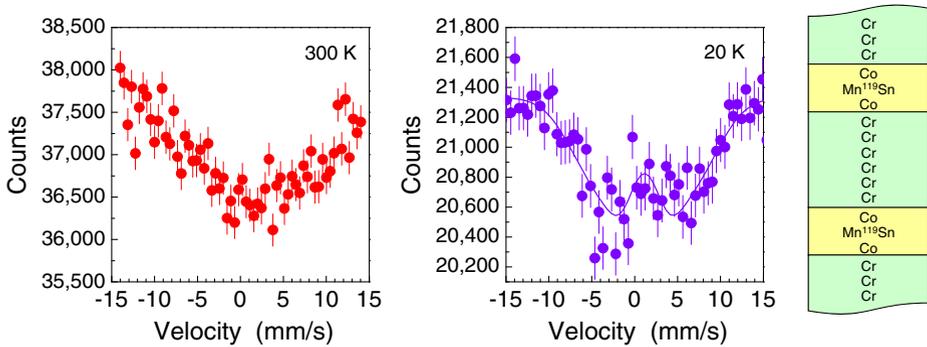


Fig. 3 Energy spectra for an ultra-thin Co_2MnSn film measured using a standard single-line CaSnO_3 absorber (See the text for details). The sample is composed of alternate stacks of $\text{Co}/\text{MnSn}/\text{Co}$ and 6 atomic layers of Cr as shown on the *right*. The corresponding time spectra are shown in Fig. 2c

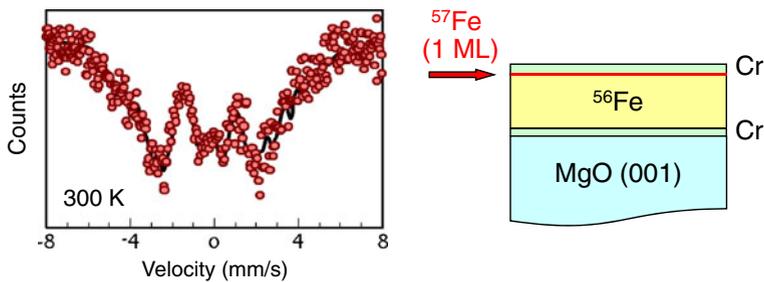


Fig. 4 Energy spectrum for the monatomic ^{57}Fe layer (1 ML) at the Fe/Cr interface measured using a $^{57}\text{FeBO}_3$ nuclear Bragg monochromator [18]. Only the interfacial Fe contains ^{57}Fe and the rest is of ^{56}Fe , as shown on the *right*

longer time than the time spectra measurement was necessary to obtain enough statistics. For better statistics, we need to optimize the thickness of the standard single-line absorber. The hyperfine field appears to be larger at low temperature, showing that the magnetization is stabilized at lower temperatures. In this way, the energy spectra give more intuitive view for the distribution of magnetic hyperfine field. Note that the advantage of this method with a standard single-line absorber is potential applicability to all the Mössbauer nuclei, including those without a useful radioactive parent [12].

When film samples contain Fe as an ingredient, the method using a $^{57}\text{FeBO}_3$ nuclear Bragg monochromator as shown in Fig. 1b can also be applicable [18, 19]. Figure 4 shows the energy spectrum for the interfacial monatomic ^{57}Fe layer of a Fe/Cr bilayer. The spectrum was obtained in 3 h. The spectrum was fitted with a distribution of hyperfine fields, which suggests that the interface is not ideally flat and that there are several sorts of interfacial Fe sites which are coordinated by different number of Cr atoms. (See ref. [18] for the details.) Note that measurements on the same kind of, but a bit thicker, enriched interfaces have been performed using conventional conversion electron Mössbauer spectroscopy [20], where it probably took several days to get good statistics.

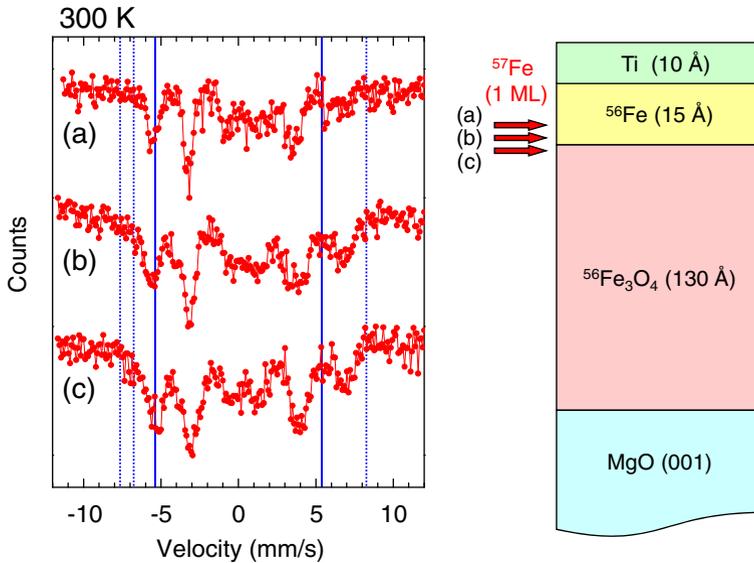


Fig. 5 Energy spectra for the monatomic ^{57}Fe layer (1 ML) near the Fe/ Fe_3O_4 interfaces measured using a $^{57}\text{FeBO}_3$ nuclear Bragg monochromator; **a** the 2nd interfacial atomic layer of the Fe layer, **b** the 1st interfacial atomic layer of the Fe layer, and **c** the 1st interfacial atomic layer of the Fe_3O_4 layer. Only the interfacial atomic Fe layer contains ^{57}Fe and the rest is of ^{56}Fe , as shown on the right. In the spectra, the positions of the 1st and 6th absorption peaks of bulk Fe are shown by the vertical solid lines and those for bulk Fe_3O_4 are shown by the broken lines. The measurement time was around 20 h and the effect is about 1 % for each spectrum

The method with a nuclear Bragg monochromator was applied also to the interfacial monatomic ^{57}Fe layer of Fe/ Fe_3O_4 . This bilayer system shows strong antiparallel magnetic coupling [9], and is promising as a “Ru-free” alternative for the antiparallel magnetic coupling system through a Ru thin layer [21] which are now used in the field of magnetic recording and spintronics. The coupling mechanism of the Fe/ Fe_3O_4 system, however, cannot be explained if ideally flat interface is assumed [22]. Therefore, it is necessary to investigate the local structures and magnetism at the buried interface to know the coupling mechanism. Figure 5 shows the ^{57}Fe energy spectra of (a) the 2nd interfacial atomic layer of the Fe layer, (b) the 1st interfacial atomic layer of the Fe layer, and (c) the 1st interfacial atomic layer of the Fe_3O_4 layer measured using a nuclear Bragg monochromator. We can obtain several pieces of information from the spectra. First, the spectra are complicated, suggesting that the interface is not atomically sharp and many different Fe sites exist around the interface. The spectra were, however, reproducible among different samples with the same structural design. Second, the components from bulk Fe or Fe_3O_4 were not observed, and the major component, with the isomer shift $\delta \sim 0.6$ mm/s and the magnetic hyperfine field $B_{\text{hf}} \sim 40$ T, comes probably from the Fe sites partially surrounded by O atoms. The detail of the analysis will be published elsewhere after additional experiments.

Synchrotron-radiation-based Mössbauer spectroscopy also opens up a possibility to measure spectra of films on thick substrates under a magnetic field at low temperatures. Figure 6 shows an example for measurements on epitaxial γ' - Fe_4N (200 nm)

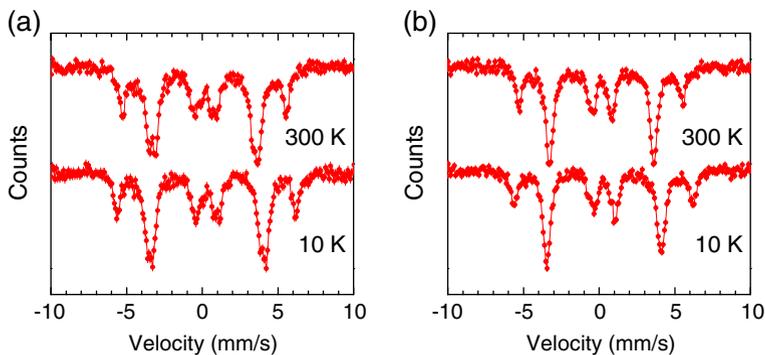


Fig. 6 Energy spectra for Fe_4N films measured using a standard single-line $\text{K}_2\text{Mg}[\text{}^{57}\text{Fe}(\text{CN})_6]$ absorber. A magnetic field of 0.3 T was applied **a** along the [100] direction and **b** along the [110] direction in the film plane. The measurement time was around 20 h and the effect is about 8 % for each spectrum

films using the method with a standard single-line absorber. Fe_4N is a ferromagnet with a cubic structure, and recently predicted [23] and confirmed [11, 24, 25] to be a material with negative spin polarization, i.e. the electric conductance is governed by the electrons in the minority spin band. The anisotropic magnetoresistance (AMR) effect, which is defined as $(\rho_{\parallel} - \rho_{\perp})/\rho_{\perp}$ (where ρ_{\parallel} and ρ_{\perp} are the resistivities when the magnetic field is applied in parallel and perpendicular to the electric current, respectively), is also negative, in contrast with usual ferromagnetic metals. Moreover, it is found that the AMR effect changes drastically at around 50 K, and that the temperature-dependent change in epitaxial (001) films is larger when the electric current is along the [100] direction than along the [110] direction [11]. Since the AMR effect originates from spin-orbit interaction in the conduction electrons, some anomaly might occur in the $3d$ orbitals at around 50 K. It is reported that the Mössbauer spectrum of epitaxial Fe_4N films at room temperature is composed of three magnetic sextets, reflecting the local environments of Fe [26]. Therefore, it is of interest to measure the spectra at low temperatures and also under an external magnetic field. Figure 6 shows the spectra at 300 and 10 K. In the measurements, an energy dip was created by a standard single-line absorber, $\text{K}_2\text{Mg}[\text{}^{57}\text{Fe}(\text{CN})_6]$. The magnetic field of 0.3 T was applied in the film plane along the incident beam by an electromagnet, and the $\text{Fe}_4\text{N}(001)$ film was set with (a) the [100] direction or (b) the [110] direction along the magnetic field. The spectrum is composed of three magnetically split components. The intensity ratio of each sextet is 3:0:1:1:0:3, due to the polarization feature of the light source and selection rule in the nuclear transitions. The shapes of the spectra differ a little between the two measurement geometries since the angle between the principal axes of the electric field gradient and the magnetic hyperfine field is different between the two. On the other hand, perceptible temperature dependence was not observed in the spectra, except for a small increase in magnetic hyperfine field at low temperature. Although the detail will be published elsewhere, we stress here that such experiments become possible for thin films for the sake of the development of synchrotron-radiation-based Mössbauer spectroscopy in energy domain.

4 Summary

The recent development of synchrotron-radiation-based Mössbauer spectroscopy opens up new aspects in the studies on thin films including those for spintronics-related materials. The techniques are now shifting from the development and demonstration phase to the application phase for material researches.

Acknowledgements The measurements in the energy domain using a nuclear Bragg monochromator were performed at BL11XU in SPring-8 (Proposal number 2011B3501, 2012A3512) and those in the time domain and those in the energy domain using a standard single-line absorber were performed at BL09XU (Proposal number 2008B1386, 2009A1375, 2009B1395, 2010A1503, 2010B1386). These works were financially supported by Core Research for Evolutional Science and Technology (CREST) Project of Japan Science and Technology Agency (JST), Element Science and Technology Project from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and Grants-in-Aid for Scientific Research on Priority Areas, for Scientific Research on Innovative Areas, and for Scientific Research (C) and (S) from Japan Society for the Promotion of Science (JSPS) and MEXT, Japan.

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