Interfaces in Sequence Permutated Multilayers

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Abstract. Sequence permutation of three building block multilayers was recently suggested as a new approach in studying bottom and top interfaces formed of a given layer with either of the other two elements. It was applied to Fe-B-Ag multilayers with 5 nm Ag layers separating the Fe and the B layers. Now we examine the dependence of the chemical mixing and the consequent amorphous phase formation on the nominal thickness of the Ag layers in [2 nm B / 2nm Fe / x nm Ag]₄, 0.2≤x≤10, multilayers. The ratio of the non-alloyed Fe layer and the amorphous Fe-B interface compound changes only below x=5 nm. It is attributed to discontinuities of the Ag layer due to its three dimensional island growth over the bcc-Fe layer. The results obtained on the variation of the hyperfine field distribution of the amorphous Fe-B layers also confirm that the top interfaces of Fe with B are more B-rich than the bottom ones.

1. Introduction

Mössbauer spectroscopy (MS) being sensitive to the local neighborhood of the Mössbauer isotope is widely used to study nanoscale multilayers. The $^{57}$Fe marker method, when the position of a thin $^{57}$Fe layer is varied across the natural Fe layer, detected differences of the bottom and the top interface [1] in several multilayer structures. The application of the above method is limited by possible mixing and diffusion between the $^{57}$Fe and the natural Fe layers. A new approach, sequence permutation of three building block multilayers [2], was suggested recently. In order to distinguish the bottom and top interfaces of the Fe layer a third element is interleaved, and the multilayers composed of three different elemental layers are deposited by sequence permutation in two different forms, as it is illustrated in figure 1. The Fe/B multilayer system was chosen [2] to be studied this way because a significant mixing of the elements accompanied by solid state amorphization occurs at the interfaces [3] already during the sample deposition and Ag was interleaved since it does not mix with either of the two elements: both Fe-Ag and B-Ag are non-mixing element pairs. The sequence permutated sample pairs can be prepared simultaneously in such a way that two of the building blocks (e.g. Fe and B, as indicated in figure 1) are evaporated together with the exception of a bottom and a top layer in the two samples, respectively. This way the accuracy of the interface analysis is greatly enhanced, since the experimental uncertainties of the layer thickness measurement can be excluded for the selected layers. Analysis of the results obtained by MS for sequence permutated sample pairs had shown [2] that the composition of the amorphous Fe/B and B/Fe interfaces are different, chemical mixing is larger at the interface where B is on top of the Fe layer.

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The layer permutation, however, influenced the sample morphology to a large extent, as it was revealed by transmission electron microscopy investigations [2]. Large interface roughness and waviness of the layers was observed when Ag was grown on top of the B layer, but B was found to grow on Ag smoothly. The Fe-Ag and Fe-B interfaces did not show such a large difference. As a consequence of the above interface properties, the variance of the Ag layer thickness was larger for the Fe/B/Ag than for the B/Fe/Ag sequence. From comparison of Mössbauer measurements on trilayer and multilayer samples the following conclusions have been drawn. In case of the B/Fe/Ag sequence the 5 nm nominal thickness Ag layers applied could be supposed to act as barriers to the diffusion between the Fe and B layers separated by them, but in case of the Fe/B/Ag sequence the variance of the Ag layer thickness allowed the mixing between them to a measurable extent. In this paper we study in more details how the thickness of the Ag layers interleaved into Fe-B multilayers influences the chemical mixing of Fe and B. In view of the above described morphological differences the B/Fe/Ag sequence was chosen for the study.

2. Experimental

The samples were prepared by thermal evaporation in a high vacuum chamber with a base pressure of $10^{-7}$ Pa onto Si(111) wafers at room temperature. Ag and B were evaporated from Cu cold crucibles by electron guns, and $^{57}$Fe was evaporated from a heated W boat. The layer thickness was measured by a quartz oscillator. The sample structures were similar to those investigated earlier [2] and illustrated in the right column of figure 1. The first layer was always 5 nm Ag and the subsequent 16 – 56 nm thick B/Fe/Ag multilayers were covered by 50 nm Ag and 100 nm B (cover layer in the followings) in order to prevent the samples from oxidation and to make them easily removable from the substrate. The layers removed were cut into smaller pieces and stacked to increase the measuring efficiency. The following samples were prepared:

Si / 5 nm Ag / [2 nm B / 2 nm $^{57}$Fe / x nm Ag]$^4$ / cover layer, with x=0.2, 0.4, 1, 2, 4, 5 and 10.

The bracket and the subscript to it indicate the multilayer unit and the number of repetitions, respectively.

The nominal layer thickness measured by the quartz oscillator was checked by transmission electron microscopy investigations in case of the x=5 sample [2]. Due to the formation of the amorphous Fe-B alloy and the amorphous (nanocrystalline) nature of the non-alloyed B (Fe) layer, the
results were not informative on the Fe and B layer thickness, but the presence of a continuous fcc-Ag layer with average thickness around 5 nm could be confirmed.

The transmission MS measurements were done with a 50 mCi $^{57}$Co–Rh source in a standard constant acceleration spectrometer. The hyperfine field (HF) distributions were evaluated according to the Hesse–Rübertsch method [4].

Figure 2. a) Room temperature Mössbauer spectra of a few selected samples of the [2 nm B / 2 nm $^{57}$Fe / x nm Ag]$_4$ multilayer series. The spectra were fitted by two crystalline sextets and a distribution hyperfine fields, as indicated for the x=10 spectrum by full, dotted, and dashed lines, respectively. b) Hyperfine field distributions with normalized area evaluated from the measured spectra as described in the text.

3. Results and Discussion
Room temperature Mössbauer spectra of a few selected samples are shown in figure 2a. The spectrum belonging to x=0 is in accordance with the results obtained earlier for Fe-B multilayers [3]. The 2 nm Fe layers are fully intermixed with B and according to the fitted HF distribution, shown in Figure 2b, it forms an amorphous alloy with a broad concentration distribution. Since the layer thickness ratio of Fe and B belongs to the Fe$_{40}$B$_{60}$ average concentration, where the magnetic moment of amorphous Fe-B
alloys disappears [5], the presence of magnetic components even at room temperature indicates that the 2 nm B layers are not fully mixed with Fe. The multilayer structure deduced from the MS results is depicted schematically in figure 3.

For x=5 and 10 the measured spectra agree within the experimental errors and can be described by two slightly broadened ($\Gamma_1=0.326(4)$ and $\Gamma_2=0.382(4)$ mm/s) sextets and a HF distribution. The two sextets (HF$_1=32.25(1)$ and HF$_2=30.24(10)$ T) can be attributed to the bulk and surface contributions of crystalline Fe layers in contact with Ag layers [6, 7], while the broad HF distribution belongs to the amorphous B/Fe interfaces [3]. According to the line intensities there are an equal number of Fe atoms that belong to the amorphous B/Fe interface and to the crystalline Fe layer. For 0<x<5 both the ratio of Fe atoms in the amorphous interface and the shape and average value of the HF distribution change continuously, while HF$_1$ and HF$_2$ remain practically constant. It is to be noted here that all the HF distributions were restricted to the range below 28.5 T in order to avoid strong correlations with the crystalline components. The variation of the spectral fraction and average HF value of the distribution is shown in figure 4. It is also worth noting that in the evaluations the close to 3:4:1:1:4:3 intensity ratio of the lines for both the crystalline and the amorphous components provided the best fit, indicating an in-plane magnetization of the samples.

Figure 3. Schematic sample structures formed by interface mixing in case of different thickness of the Ag layer in the [2 nm B / 2 nm $^{57}$Fe / x nm Ag]$_4$ multilayer series, as inferred from the Mössbauer measurements. In case of a continuous Ag layer ($x$$\geq$5) mixing of Fe and B (dashed area) takes place only at the bottom side of the Fe layer. When there is no Ag layer interleaved ($x$=0), it occurs both at the bottom and the top sides and the 2 nm Fe layer is fully amorphized. For 0<x<5 Ag islands are formed with varying area and height and protect the top side of the underlying Fe area from amorphization.

The changes observed for varying Ag layer thickness can be understood if we suppose that below 5 nm nominal thickness the Ag layer is not continuous, as it is illustrated in figure 3. In case of a continuous Ag layer (x=5 and 10) mixing of Fe and B takes place only at the bottom side of the Fe layer. In the case, however, when there is no Ag layer interleaved (x=0), it occurs both at the bottom and the top sides and the bottom and top Fe-B interfaces overlap. In between these two extremes (0<x<5) Ag islands are formed with varying area and height and the area of the Ag covered Fe layer gradually increases with x. As a consequence the ratio of bcc-Fe increases and that of the amorphous interface decreases, as it can be seen in figure 4.

In parallel with the intensity change, the shape and the average HF value of the distribution also varies, as it can be seen in figures 2b and 4. These changes are in accordance with the result obtained from the sequence permutation studies [2], the average HF is larger when the ratio of the bottom
(B/Fe) interfaces is larger in the sample. The distributions cover a broad range of HFs for all the samples, the standard deviations vary between 7.4 and 8.3 T, and the increase of the average HF is mainly the result of a decrease in the respective ratio of the low field components. The increase of the average HF, accompanied also by a decrease of the average isomer shift, can be interpreted as a decrease of the average B concentration [5] of the amorphous Fe-B interface.

Of course, the validity of the above simple model is limited. In case of very small Ag islands the lateral diffusion of Fe and B should also be taken into account and non-equilibrium mixing of Ag with either Fe or B or with the amorphous Fe-B alloy might also take place. However, it is remarkable that both the fraction and the average HF of the amorphous phase keep varying in the small Ag thickness range, as well. Since the room temperature average values might also be influenced by the presence of superparamagnetic particles, low temperature and in-field measurements are under way to analyze in more details the role of the Ag atoms in the formation of the amorphous Fe-B interface. The possible effect of the Ag neighbors on the hyperfine fields of the different components is also to be studied. Our preliminary results indicate, however, that the changes observed in the room temperature data are indeed basically due to the variation of the amount and the composition of the amorphous phase.

![Graph](image)

**Figure 4.** Spectral area (open symbols) and average HF (full symbols) of the fitted distribution as a function of the nominal Ag layer thickness. The lines are guide to the eye.

4. Conclusions
The hyperfine field distribution of the amorphous Fe-B interfaces are influenced by the Ag layer thickness in [2 nm B / 2nm Fe / \(x\) nm Ag]₄ multilayers. Since Ag does not mix with either Fe or B, the observed changes are attributed to the three dimensional island growth of Ag below 5 nm nominal thicknesses and the consequently different ratio of the B/Fe and Fe/B interfaces. The results also confirm the conclusion [2] that the bottom and the top interfaces of Fe are different in Fe-B multilayers, the top interfaces being richer in B than the bottom ones.

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