Interface properties in sequence permutated Fe–B–Ag multilayers

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Fe–B–Ag multilayers have been prepared in two different sequences of the layers in order to reveal distinctness of “top” and “bottom” interfaces of each element in relation to the other two elements. Transmission electron microscopy analysis showed a much larger interface roughness for the Fe/B/Ag (i.e., Fe at bottom, Ag on top of B) than for the B/Fe/Ag sequence, which is mainly due to the different growth processes of Ag. For both sequence Fe and B layers of 2 nm thickness are continuous and solid state amorphization—similar to that observed in Fe/B multilayers—takes place during sample growth. Mössbauer spectroscopy measurements indicate that the amorphous interface has a broad bimodal concentration distribution for both layer sequence, but intermixing is larger at the Fe/B than at the B/Fe interface. © 2009 American Institute of Physics.

I. INTRODUCTION

Multilayered magnetic materials are used in a number of technological applications such as spin valves, recording media, magnetic sensors, etc. Recently, attention is devoted to different nanogranular and amorphous alloy multilayer systems1–3 since these have advantageous magnetic properties for high frequency applications. The quality of the interface and the extent of interface mixing are essential questions for applications and may influence the amorphous phase formation in a multilayer structure. Since the interface properties largely depend on the growth mechanism (e.g., layer by layer or three dimensional) of the subsequent atomic layers, they can be very different on the bottom and the top side of each layer when the different materials are sequentially deposited over each other.4

Mössbauer spectroscopy (MS) being sensitive to the local neighborhood of the Mössbauer isotope is widely used to study nanoscale multilayers. The 57Fe marker method, when the position of a thin 57Fe layer is varied across the natural Fe layer, detected differences in the bottom and the top interface5 in several multilayer structures. The application of the above method is limited by possible mixing and diffusion between the 57Fe and the natural Fe layers. Here we present a new approach which works also for cases where diffusion and mixing of the subsequent layers take place during either sample deposition or postannealing. 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. The Fe/B multilayer system is chosen to be studied this way because a significant mixing of the elements occurs at the interfaces already during the sample deposition and Ag will be interleaved since it does not mix with either of the two elements. These multilayer structures, as it will be shown, are quite complex, as nanosize Fe grains and amorphous Fe–B alloys of different compositions are formed at the interfaces. For the interface analyses we combine 57Fe MS and transmission electron microscopy (TEM). MS can give quantitative information on the chemical mixing at the Fe–B and Fe–Ag interfaces, while TEM is able to analyze both the structure in high resolution and the larger scale morphology of all the interfaces.

In samples with different permutations of the layer sequence, each element pair has different types of interfaces, e.g., B on top or at the bottom of the Fe layer. Fe–Ag and Ag–B are nonmixing element pairs with positive heat of mixing according to their phase diagram,6 whereas Fe–B has a negative heat of mixing and a possibility for the formation of stable or metastable phases in the whole concentration range.7 According to this, a significant difference in the chemical composition of top and bottom interface can only be expected for the Fe–B interfaces, Fe/B and Fe/Ag multilayers have already been studied8–13 and they indeed show very different interface properties. In case of Fe/B multilayers the formation of an amorphous interface was reported,8,9 which exhibits a very broad and bimodal hyperfine field (HF) distribution spreading roughly over the whole range between 0 and 30 T. Superparamagnetic relaxation was excluded as a possible cause of the observed peak around 0 T and the presence of B-rich nonmagnetic components was confirmed by the application of external magnetic field at low temperature.14 Spectrum component characteristic to bulk α-Fe could only be observed when the Fe layer thickness was larger than 2 nm. The much smaller degree of interface mixing in Fe/Ag multilayers is shown by the relatively narrow distribution of the HFs, which can be characterized by two broadened sextuplets at low temperatures13 even for 0.2 nm nominal Fe layer thicknesses. At elevated temperatures the magnetic splitting may disappear if the Fe layers are discontinuous. When finite size Fe islands are formed a superparamagnetic relaxation takes place above the blocking temperature which depends on the size distribution of the islands. However at low temperatures, paramagnetic Fe atoms can only be observed at extremely small Fe

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concentrations.\textsuperscript{15,16} Multilayers of Ag and B were studied as they are good candidates for extreme ultraviolet mirrors, but since they were reported to form very poor multilayer structures,\textsuperscript{17} extensive investigations have not been done. The pronounced island growth of Ag over B was shown\textsuperscript{17} to result in surface roughness comparable to or larger than the nominal layer thickness.

The largely different interface properties of Fe/B and Fe/Ag multilayers are illustrated in Fig. 1 by samples where the interface contribution is significant. In both cases two sextets were allowed in the evaluation for the well resolved magnetic component. Further on, a broad distribution of HF s was necessary to describe the Fe–B and a paramagnetic doublet to fit the Fe–Ag multilayer spectra. The broad distribution of HF s can be associated to the amorphous Fe–B interface. The sextet with larger intensity and magnetic splitting can be attributed to Fe atoms in a crystalline Fe layer without B or Ag neighbors, i.e., inside the layer. The second sextet with smaller intensity and magnetic splitting belongs to Fe atoms in a crystalline Fe layer with B or Ag neighbors, i.e., inside the layer. The second sextet can be attributed to Fe atoms in a crystalline Fe layer without B or Ag neighbors, i.e., inside the layer. The second sextet can be attributed to Fe atoms in a crystalline Fe layer without B or Ag neighbors, i.e., inside the layer.

In the above notation the brackets contain the multilayer unit and the number in subscript shows the number of repetitions. The A- and B-type samples having similar layers in different sequence have been prepared together in a way that the Fe layers (with the exception of the first Fe layer of B-type samples and the last Fe layer of A-type samples) and the Ag layers were evaporated simultaneously, while during the evaporation of the B layers one of the samples was behind a shutter.

The paramagnetic doublet in the Fe–Ag sample belongs to an oxide phase containing a few percent of the Fe atoms. It is also worth noting that in the evaluations the 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.

This paper will be organized as follows. First the results of TEM measurements will be presented. Since the diffraction patterns of the different phases (of bcc-Fe and fcc-Ag or of amorphous B and amorphous Fe–B alloys) strongly overlap, conclusions will be drawn mainly on the morphology of the layers. Next we will present the Mössbauer results, where first the temperature and external magnetic field dependence of the spectra will be examined in order to decide if the spectra are influenced by superparamagnetic relaxation. Conclusions on chemical mixing at the Fe–B interface will be drawn from measurements at low temperature or in external magnetic field. To account for the observed layer sequence dependent mixing two possible explanations will be discussed: the difference of sample morphology revealed by the TEM measurements and the relative positions of the Fe and B layers. Finally, a comparison will be made between trilayer and multilayer samples in order to clarify the respective role of the above two factors.

II. EXPERIMENTAL

The samples were prepared by thermal evaporation in a high vacuum chamber with base pressure of $10^{-7}$ Pa onto 2 in. 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 nominal layer thickness was calculated from the bulk densities and the mass measured during evaporation by a quartz oscillator. In case of the samples prepared for MS studies the first layer was always 5 nm Ag and the subsequent 30–40 nm thick Fe–B–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 substrate. The layers were removed with the help of a scotch tape, cut into smaller pieces, and stacked to increase the measuring efficiency. Two sample pairs with different Fe and B thickness have been prepared this way with the following multilayer sequences:

\begin{equation} \text{Si}/[5 \text{ nm } \text{Ag}/2 \text{ nm } ^{57}\text{Fe}/2 \text{ nm } \text{B}]_{n}/\text{cover layer}, \quad (\text{A1}) \end{equation}

\begin{equation} \text{Si}/[5 \text{ nm } \text{Ag}/2 \text{ nm } \text{B}/2 \text{ nm } ^{57}\text{Fe}]_{n}/\text{cover layer}, \quad (\text{B1}) \end{equation}

\begin{equation} \text{Si}/[5 \text{ nm } \text{Ag}/1 \text{ nm } ^{57}\text{Fe}/1 \text{ nm } \text{B}]_{n}/\text{cover layer}, \quad (\text{A2}) \end{equation}

\begin{equation} \text{Si}/[5 \text{ nm } \text{Ag}/1 \text{ nm } \text{B}/1 \text{ nm } ^{57}\text{Fe}]_{n}/\text{cover layer}. \quad (\text{B2}) \end{equation}

In the above notation the brackets contain the multilayer unit and the number in subscript shows the number of repetitions. The A- and B-type samples having similar layers in different sequence have been prepared together in a way that the Fe layers (with the exception of the first Fe layer of B-type samples and the last Fe layer of A-type samples) and the Ag layers were evaporated simultaneously, while during the evaporation of the B layers one of the samples was behind a shutter.
Since the sample thinning was unsuccessful for the above samples, multilayers similar to A1 and B1 were prepared for electron microscopy investigations with the difference that it contained natural Fe, the first layer was 2 nm B, and the cover layer was only 5 nm Ag.

\[ \text{Si/2 nm B/}[2 \text{ nm B/5 nm Ag/2 nm Fe}]_4/5 \text{ nm Ag}, \quad (A1) \]

\[ \text{Si/2 nm B/}[2 \text{ nm Fe/5 nm Ag/2 nm B}]_4/5 \text{ nm Ag}. \quad (B1) \]

Cross-sectional samples for TEM analysis were made in a conventional manner, i.e., face-to-face gluing, mechanical polishing and Ar\(^+\) ion-beam milling with a Gatan Precision Ion Polishing System. As the interface structure of the multilayers is heat sensitive, extra care was taken to reduce the heat load of the specimens during the preparation process. High resolution analysis of the samples were made by a 300 kV microscope with field-emission gun (JEOL 3000F). Chemical element sensitive mapping of the layers was done by electron energy loss spectroscopy (EELS) analysis with a postcolumn Gatan Imaging Filter (Tridiem model) attached to a 3010 JEOL electron microscope. The three-window technique was applied to get the net element-selective images.

The transmission MS measurements were done with a 50 mCi \( ^{57}\text{Co–Rh} \) source in a standard constant acceleration spectrometer. Isomer shift (IS) is given relative to \( ^{\alpha}\text{Fe} \) at room temperature. The measurements in external magnetic field were performed in a Janis cryostat equipped with a superconducting magnet generating magnetic field parallel to the \( \gamma \)-ray direction. The HF distributions were evaluated according to the Hesse–Rübertsch method.\(^{18} \)

III. RESULTS AND DISCUSSION

TEM micrographs of samples A1 and B1 are shown in Figs. 2(a) and 2(b). Continuous layers can be observed in both samples, but the layer structure is very different for the two cases. Obviously, the interface roughness in sample A1 is much larger than in sample B1. The large difference should be due to the different sequences of the deposited Ag and B in the samples. TEM investigation of Fe–B\(^4\) and Fe–Ag\(^{12}\) multilayers have not observed anomalously large interface roughness or significant difference of bottom and top interfaces. The large interface roughness in case of A1, where Ag is grown on top of the B layer, is in accordance with the ***in situ*** x-ray photoelectron spectroscopy observation\(^{17} \) that the coverage of the B substrate by Ag increases very slowly with the nominal Ag layer thickness. It was attributed to the island formation\(^ {17} \) of Ag when grown over B.

The layer formation in the two samples was inspected by high resolution TEM (HRTEM) [Figs. 2(c) and 2(d)] and element sensitive EELS mapping (Fig. 3). The deposited materials give different contrasts in the HRTEM images resulting from their dissimilar densities. According to this, the Ag appears in a darkest contrast. Large defect free crystallites of Ag can be observed in sample B1 whereas in sample A1 the Ag layer is composed of smaller crystallites and forms an irregular layer of nonuniform thickness. We observed parallel crystalline lattice fringes in successive Fe and Ag phases suggesting local epitaxial growth of Ag on Fe in a few regions of sample B1 (Fe/Ag interface), but no such regions could be found in A1 (Ag/Fe interface). The epitaxial relation observed in B1 is similar to that found in Fe/Ag multilayers\(^{12} \) and the lack of such observation in A1 might be due to the much larger variation of crystallite orientation and the smaller grain size of Ag in this sample. EELS based elemental mapping was performed to localize the individual elements within the multilayer. Fe-\( L_{2,3} \) edge) and B-\( K \)-edge) maps of sample A1 [Figs. 3(b) and 3(c)] are compared to a HRTEM image [Fig. 3(a)] of the same area. The growth of the layers could be understood by using the marked reference area in each image. The deposited Ag forms equiaxed grains, typically around 5–10 nm in diameter on top of the amorphous B layer. By coalescence these grains form a more or less continuous layer with a rough and irregular surface. The surface irregularities of the Ag layer are rather uniformly followed by the growing Fe and B layers and their shapes seen on the elemental maps match with each other, as well, as with the high resolution image. It should, however, be noted that the Fe deposited over the rough Ag surface grew in much smaller grains and filled some small gaps between the Ag crystals. Although not experimentally verified, it is possible that in some areas pinholes exist in the Ag layer and the deposited Fe atoms can intermix with the first deposited B layer forming an amorphous B–Fe area below the Ag crystals.

The growth mode of an element over another one is determined by the surface and the interface energies and there can be large differences in the growth mode when substrate and overlayer are reversed.\(^{3} \) This way it is possible that B can grow smoothly over Ag and although B–Ag\(^ {17} \) and Fe/B/Ag multilayers are of poor quality, Fe/Ag/B multilayers...
have much more regular layer structure. The very different sample morphologies shown are due to the different growth mode of the Ag layer over B in A1 and over Fe in B1, as it was explained above. One has to note here that the properties of the starting layer may to some extent influence the growth and morphology of the multilayers and that way the properties of the sample set for Mössbauer measurements might be slightly different. The different growths of Ag over B and Fe in case of the two different sequences are, however, maintained through the multilayer structure supporting our view that the difference in morphology basically stems in the different layer sequence. The layers indicated as Fe and B in

![Fig. 3](image3.jpg)  
**Fig. 3.** HRTEM image (top) and energy filtered EELS map of the Fe (middle) and the B (bottom) distribution in a selected area of sample A1.

Fig. 2 do not show this large difference in the two samples, both being rather disordered. It is, however, important to note here that as it will be revealed by the MS results the layers of different contrasts do not belong to pure Fe and B, but rather to Fe-rich and B-rich regions. Crystalline order cannot be observed in the B-rich layers, but in case of the darker Fe-rich layers crystallites of very small size as well as disordered regions can be observed. Due to the very small crystal size, the distribution of crystal orientations, and the significant amount of disorder a true distinction between nanocrystalline and amorphous regions cannot be made even at this high resolution.

Electron diffraction and selected area diffraction pattern technique were also applied to reveal the various phases within the cross sectional multilayer samples. The diffraction patterns of the two samples are very similar and that of sample B1 is shown in Fig. 4(a). Beside the single crystal spots of the silicon substrate the characteristic ring pattern of the polycrystalline Ag phase (mainly randomly oriented with some 111 texture) can be seen. Since all the reflections of bcc-Fe phase fall on Ag diffraction rings, the presence of bcc-Fe cannot be proved this way. Some extra spots within the first Ag ring were observed too, which can be either attributed to the 110 and 020 reflections of the stable tetragonal FeB phase or to a higher order Laue zone of the Si substrate (visible due to multiple scattering). Thus the presence of any crystalline Fe–B phase cannot be inferred from the electron diffraction pattern. Several diffuse rings of one or more amorphous phases can also be observed in the electron diffraction patterns. The amorphous component forms irregular layers as it can be seen on the dark field image of Fig. 4(b), which was taken with the objective aperture lying completely inside the first Ag ring, but the separation of amorphous B and amorphous Fe–B alloys is not possible in such very thin films.

Room temperature Mössbauer spectra and the evaluated HF distributions of the two sample pairs are shown in Fig. 5. In case of samples A1 and B1 the HF distributions stretch from zero up to 33 T, the value of the HF in pure $\alpha$-Fe. The line intensities of the magnetic sextets are 3:4:1:1:4:3, indicating an in-plane orientation of the magnetization, which in polycrystalline thin films generally results from the shape anisotropy. Quadrupole splitting (QS) of the individual sex-
The spectra of Fe\textsubscript{48}B\textsubscript{80} average composition which is nonmagnetic when prepared as a homogeneous alloy\textsuperscript{20,23} by codeposition. The gradually increasing ratio of the magnetic components and the broad HF distribution at low temperatures may indicate a broad concentration distribution of the amorphous matrix formed by solid state diffusion,\textsuperscript{8} but superparamagnetic relaxation of different size small magnetic particles might also contribute to the observed temperature dependence.

To overcome the problems caused by a possible magnetic relaxation, samples A1 and B1 have been measured at 150 K applying 3 T external field and these spectra are shown in Fig. 7. Since the magnetic field was parallel to the \(\gamma\)-ray direction, the 3:0:1:1:3 intensity ratios apply to the magnetic sextets above the demagnetization field (2.2 T for pure \(\alpha\)-Fe). This way, application of an external field has the further advantage that the HF distribution of the amorphous phase is better resolved and not perturbed by correlations.

### Figure 5

Room temperature Mössbauer spectra of the sequence permuted sample pairs. The normalized HF distributions are also shown for each spectrum on the \(x=0\)–30 T and \(y=(0–16) \times 10^{-2} \text{T}^{-1}\) scales. For the A2 sample the \(y\) scaling is an order of magnitude larger and an evaluation with two single lines is also shown.

### Figure 6

Mössbauer spectra of samples A2 and B2 measured at low temperatures. The normalized HF distributions are also shown for each spectrum on the \(x=0\)–30 T and \(y=(0–16) \times 10^{-2} \text{T}^{-1}\) scales.

### Figure 7

(Color online) Mössbauer spectra of the sequence permuted sample pairs A1 and B1 measured at 150 K in 3 T external fields applied parallel to the \(\gamma\)-ray direction. The spectra were fitted with two sextets (bulk and surface component of the crystalline Fe layer indicated by blue and green colors) and a distribution of HFs (amorphous Fe–B interface indicated by red color). The fitted bimodal HF distributions are also shown for both spectra.
with the intensities of the second and fifth lines. The measured spectra could be evaluated by two separate sextets and a HF distribution; these subspectra are also indicated in Fig. 7. The three subspectra represent Fe atoms inside a pure Fe layer, at the Ag/Fe (A1) or Fe/Ag (B1) interface and in the amorphous phase formed at the Fe/B (A1) or B/Fe (B1) interface.

Comparing the results for the two samples the largest difference can be found in the shape of the HF distributions also shown in Fig. 7. Although both show a relatively sharp low field peak and a broader one in the 10–25 T range, the ratio of these peaks is very different. The low field peak covers about 60% of the whole HF distribution in case of A1, while this number is only about 30% for B1. This difference can be well seen in the measured spectra as there are very different absorption intensities around the zero velocity. The low field peak belongs to paramagnetic or nonmagnetic Fe atoms as it is explained for the room temperature spectra. As nonmagnetic Fe–B crystalline compound phases are not known, it should belong to an amorphous phase which is nonmagnetic or has a Curie temperature below 150 K. These conditions indicate that the average B content of this portion of the Fe/B interface should be above 55 at. %. The broad second peak covers the HF range of the different stable and metastable crystalline compounds, FeB, Fe2B, and Fe3B, but it probably also belongs to amorphous regions as sharp lines cannot be observed. The absence of crystalline Fe–B components is in line with the electron diffraction results. It should be noted that the HF distribution stretches up to 30 T in Fe–B multilayers (see Fig. 1), but since in this range it strongly correlates with the smaller intensity crystalline component, the HF distribution was limited at 25 T. The second peak of the HF distribution is more smeared out for A1 than for B1, which definitely shows a peak around 20 T and a higher average value. All these differences result in a largely different average value of the HF distributions, 9.5 and 13.8 T for A1 and B1, respectively. In summary, the in-field MS results, both the higher percent of nonmagnetic Fe atoms and the smaller average HF field of the magnetic components, definitely show that the average B concentration of the amorphous phase is higher at the Fe/B than at B/Fe interface.

The two crystalline sextets in Fig. 7 can be attributed to Fe atoms inside a crystalline Fe layer and at the surface of it in contact with the Ag and the amorphous Fe–B layer. The fitted parameters, HF=32.0 and 28.4 T, IS=0.11 and 0.25 mm/s for A1 and HF=32.5 and 28.7 T, IS=0.09 and 0.27 mm/s for B1 are in agreement with that measured for the Fe/Ag multilayer of Fig. 1 at this temperature and magnetic field, HF=32.3 and 29.3 T, IS=0.11 and 0.29. In external field, when all the magnetic moments are aligned, the internal field is reduced by the value of the applied field and increased by the demagnetization field. This way the larger splitting is roughly equal to the value measured for bulk Fe with 33 T HF. (It is slightly higher than that if the demagnetization field is smaller than 2 T.) The component with lower HF can be mainly attributed to Fe atoms at the Ag/Fe (A1) and Fe/Ag (B1) interface according to its large positive IS, but the differences in the hyperfine parameters are close to the experimental errors, i.e., significant conclusion cannot be drawn on the difference of the Ag/Fe and Fe/Ag interfaces.

From the intensity of the crystalline components in Fig. 7 the thickness of the nonalloyed Fe layer can be estimated. The two crystalline components cover 50% and 63% of the total area under the spectra for A1 and B1, respectively. From the above percentages and from the 2 nm nominal thickness of the deposited Fe the thickness of the crystalline Fe layer can be calculated as 1 and 1.2 nm for A1 and B1, respectively. (The 13% difference in the intensities is in the order of the experimental errors, but might also indicate a larger mixing at the Fe/B than at the B/Fe interface.) Both values are definitely smaller than the average thickness of the layer indicated as the Fe layer in Fig. 2. Due to the large fraction of the amorphous Fe–B phase the pure B layer should also be significantly less than 2 nm. (Estimating the average B concentration of the amorphous Fe–B fraction from the MS data is not feasible since in both samples there is a large fraction of nonmagnetic Fe atoms.) From this analysis it is evident that the layers which can be seen in the TEM pictures of Fig. 2 do not belong to elemental layers of Fe and B, the approximately 2 nm thick darker and lighter contrast layers should rather be Fe- and B-rich regions. Due to the nanocrystalline structure of the nonmixed Fe layer and the amorphous structure of evaporated B, the border lines of the amorphous Fe–B layer cannot be well recognized.

Although the low temperature and the in-field MS results undoubtedly show that the B concentration distributions of the Fe–B interfaces are different in the sequence permuted sample pairs of Fe–B–Ag multilayers, the question, to what extent the difference can be due to the different waviness of the interleaved Ag layers, still remains to answer. On one hand, the EELS measurements presented in Fig. 3 indicate that shadowing effect does not significantly modifies the B and Fe layer growth and both follow nicely the irregularities of the thick Ag layer. On the other hand, the larger variance of the Ag layer thickness can influence the degree of mixing between the Fe and the B layers. At those sites where the interleaved Ag layer is missing the 2 nm Fe layer can be fully alloyed with B, as it was observed in Fe/B multilayers. In case of a thin Ag layer diffusion of B or Fe through pinholes can modify the composition of the amorphous matrix. To exclude these effects, a pair of trilayer samples were prepared, i.e., the same as A1 and B1, but the repetition number was 1. In this case Ag is grown over B only as a cover layer in sample A1 and cannot disturb the Fe/B interface formation.

The 12 K spectra of the trilayer and the multilayer samples and the evaluated HF distribution of the amorphous interface are shown in Fig. 8. Superparamagnetic component is not expected at this low temperature. Similarly to the in-field measurements shown in Fig. 7, the spectra were fitted with two crystalline sextets and a distribution of HFs. The amplitude ratio of 3:4:1:1:4:3 was allowed both for the crystalline and the amorphous components. In case of A1 and the respective trilayer sample the presence of a small oxide component (with 2% and 7% of the Fe atoms) was obvious and was taken into account in the fitting for a third crystalline sextet. As it can be seen in Fig. 8 the HF distribution of the
amorphous interface depends on the layer sequence in the trilayer samples similarly to that what can be observed for the multilayer sample pair. The ratio of the small field components of the HF is larger in case of the Ag/Fe/B than in case of the Ag/Fe/B/sequence both for the trilayer and the multilayer samples. The average HF value of the distributions reflects this difference; it is 12.2 and 16.5 T for the multilayer and 13.7 and 15.8 T for the trilayer samples with Ag/Fe/B and Ag/B/Fe sequence, respectively. The difference in the average HF values is smaller for the trilayer sample pair (2.1 T) than for the multilayer one (4.3 T), showing that in the multilayer samples the Fe–B intermixing is indeed influenced to some extent by the morphology of the interleaved Ag layers. The main effect, however, is the different chemical mixing at the Fe/B and B/Fe interfaces. The large difference in the measured spectra around the zero velocity both for the trilayer and the multilayer sample pairs gives a direct evidence of this statement. According to the calculated average HF values there is an at least 4 at. % difference of the average B concentration\(^20\) of top and bottom interfaces.

Diffusion amorphization is expected to occur in systems with negative heat of mixing and significantly different diffusion rates of the components.\(^24\) After an initial stage, the relevant diffusion rates are those characteristic to the diffusion in the structures formed during the intermixing process. In some metallic glasses the order of magnitude of the diffusion constant of B was found to be similar\(^25\) or slightly larger\(^26\) than that of Fe, but diffusion through grain boundaries or at the surface of the growing layer can be quite different than that in the bulk. The difference in the Fe/B and B/Fe interfaces is either explained by a different diffusion mechanism for the two cases or by a different heat transfer from the source during evaporation due to the different melting points. In any case the observation of a bimodal concentration distribution at the amorphous interface, as can be deduced from the HF distribution, is an unexpected result since the calculated free energy of the amorphous phase\(^7\) has a single minimum at around 40 at. % B. The bimodal concentration distribution might explain the relatively sharp border between the B- and Fe-rich amorphous layers observed in the TEM picture of Fig. 2.

In summarizing the results, Fe/B/Ag and B/Fe/Ag multilayers were prepared and studied for the first time and the layer sequence permutation was introduced as a novel method to study the distinctness of top and bottom interfaces of the elemental layers. Analysis of the results obtained by MS for sequence permuted sample pairs shows 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. Although in both cases a broad bimodal HF distribution is observed, the low field peak—belonging to high B concentration amorphous Fe–B alloys—has a higher proportion for the Fe/B than for the B/Fe interfaces. TEM investigations revealed that layer permutation influences the sample morphology to a large extent. On one hand, pronounced island growth of Ag on B was observed which obstacles preparing B/Ag or Fe/B/Ag multilayers with small interface roughness. On the other hand, B was found to grow on Ag smoothly and the B/Fe/Ag sequence is more favorable for multilayer preparation. The larger variance of the Ag layer thickness in case of the Fe/B/Ag sequence can only partly explain the stronger chemical mixing between the Fe and the B layers for the above sequence of the layers. The Mössbauer measurements on Ag/Fe/B and Ag/B/Fe trilayer samples show that a significant difference in interface mixing arises merely from the different sequence of the Fe and B layers, i.e., top and bottom interfaces of Fe with B are different. The overall morphological and chemical differences observed in the multilayer samples indicate for applications that layer sequence permutation can be an effective tool of tailoring multilayer properties.

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