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Mössbauer investigation of the growth of the Fe multilayer in Fe(100)/Ag(100) structures

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A monolayer of ^{57}Fe is used as a probe layer in molecular-beam-epitaxy-grown Ag/Fe(001)/Ag(001) structures. Different Fe sites can be distinguished in the iron multilayer based on the isomer-shift (i.s.) and quadrupole-splitting (QS) values of different components in the Mössbauer spectrum. This makes it possible to determine the concentration of ^{57}Fe atoms in the different atomic Fe layers and obtain information about the growth processes for different regions of the Fe multilayer. It was found that after deposition of about 5-Fe ML the growth changes from a Fe multilayer formation mode to a quasi-layer-by-layer mode. The values of the i.s. and QS are the same for Fe atoms located at the top and bottom Ag/Fe interface. H_{hf} values, on the other hand, are different by 9 kOe at the top and bottom for a sample in which the upper Ag(001) layer is covered by another Fe(001) layer. This result may be due to a contribution to the top H_{hf} value from Ruderman-Kittel-Kasuya-Yosida-like spin-density oscillations that couple the ferromagnetic Fe multilayers across the nonmagnetic Ag spacer.

I. INTRODUCTION

The molecular-beam-epitaxy (MBE) technique makes it possible to create metallic ultrathin structures that are of great interest for the study of low dimensional systems. Over the years, it has become clear that the growth and structure of MBE-grown samples has caused controversy between different laboratories. Samples are grown on different substrates, different techniques are used for monitoring the growth and the results of the growth are often very different. It is important to realize that no technique for monitoring the deposition of atomic layers has sure answers about all the phases of the growth process. The more techniques are combined for studying the growth of MBE samples, the more complete the picture is that can be obtained.

The growth of samples prepared by MBE is usually monitored by using techniques such as reflection high-energy electron diffraction (RHEED), low-energy electron diffraction, and Auger-electron spectroscopy. These techniques are employed for studying the surface while the deposition of new atomic layers takes place. Scanning tunneling microscopy (STM), field-ion microscopy, and low-energy ion scattering can also be used to study the surface of the samples. In the present study, we will show how Mössbauer-effect-spectroscopy (MES) can provide confirmation of previous interpretations of the growth process based on techniques such as RHEED, and also that MES provides information that cannot be obtained by previous techniques. We will demonstrate this by applying MES to MBE-grown Ag(100)/Fe/Ag structures.

For iron, the Mössbauer effect is only observed for the ^{57}Fe isotope. The MBE-grown structures generally consists of a few very thin Fe films. Because natural iron contains only 2% ^{57}Fe, the MES studies are often performed on samples with Fe films that are close to 100% enriched in ^{57}Fe. This reduces the data collection time considerably. The values of the isomer shift (i.s.), magnetic hyperfine field H_{hf}, and quadrupole splitting (QS) that are measured by MES depend on the local charge- and spin-density and the local electric-field gradient. As such MES can give information with atomic scale resolution about the Fe sites in Ag/Fe structures, unless too many Fe sites are present for which the components in the spectrum are not adequately resolved.

In an early MES investigation of Ag(100)/Fe/Ag structures, Fe multilayers consisting entirely of enriched ^{57}Fe were deposited.[1] In that study, all the possible Fe sites in the Fe multilayer were sampled at the same time. The spectra showed very broad lines indicating that many Fe sites are present in the Fe multilayers. The individual components in the spectra that are associated with these sites could not be resolved. Nevertheless, the spectra could tentatively be fitted with two components that were associated with Fe sites located at the Fe/Ag interface and Fe sites in the interior of the Fe multilayer, respectively.

Calculations for an ideal nonterraced Fe multilayer by Ohnishi, Weinert, and Freeman[2] showed that each atomic layer (ML) in a thin film represents a unique Fe site. The values of H_{hf} and to a lesser extent also the values of i.s. depend on how many atomic layers the ^{57}Fe is removed from the Ag/Fe interface. In order to verify this, one can grow probe layers of ^{57}Fe at specific locations in the Fe films of the samples. If this is done successfully, then MES gives the i.s., QS, and H_{hf} values for that location. This was attempted in MES studies of the Ag(100)/Fe structure where a probe layer consisting of two ^{57}Fe monolayers was used.[3,4] However, the growth of new atomic layers takes place on a terraced substrate. As a result, the deposition of the equivalent of 2-ML ^{57}Fe

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actually distributes ^{57}Fe atoms in three or even more different atomic layers in the Fe multilayer if the growth is not layer by layer. In addition, for ^{57}Fe atoms at a terraced Ag/Fe interface, we can identify at least three Fe sites when only nearest-neighbor (NN) Fe and Ag atoms are taken into account (Fig. 1). It is perhaps not surprising, therefore, that the 2-ML ^{57}Fe probe layer MES studies just showed broadened structureless peaks and did not provide a significant improvement in the resolution compared to the previous measurement[1] where the complete Fe multilayer consisted of ^{57}Fe.

Recent MES studies[5,6] of the Fe multilayer in Ag/Fe/Ag structures where only one ^{57}Fe atomic layer was used as a probe layer showed much better resolution. The study of Liu and Gradmann[5] of W(001)/40Fe/Ag structures could measure the MES parameters for each individual Fe atomic layer except in the vicinity of the Fe/Ag interface. Our conversion electron Mössbauer effect spectroscopy (CEMS) study of the Fe(001)/Ag(001) interface in MBE-grown Ag/(5.7Fe/1^{57}Fe/10Ag)$_3$/9Au using 1 ML of ^{57}Fe as a probe layer could clearly distinguish between Fe sites located at the interface and those Fe atoms that do not make contact with Ag atoms.[6] In addition, three Fe sites that are related to the nearest neighbor configuration at the Fe/Ag interface could be identified in the MES study. The three sites are due to the existence of terraces at the top (Ag on ^{57}Fe) interface (Fig. 1). Site I Fe atoms refer to Fe positions in the central region of the terraces. Sites I_t and I_b refer to atoms located at the edge of the Fe terraces, i.e., at the top and the bottom, respectively. Because of the different configurations of Fe and Ag neighbors, the i.s. and QS values for the Fe sites I, I_t, and I_b are slightly different from each other and significantly different from those obtained for ^{57}Fe atoms that are one or more atomic layers removed from the Ag/Fe interface, e.g., at Fe sties II and III (Fig. 1).

The possibility of identifying the Fe sites in the Mössbauer spectrum makes MES a useful tool for studying the growth process of MBE samples. When the equivalence of 1-ML ^{57}Fe is deposited, the actual distribution of ^{57}Fe over different Fe sites in the multilayer can be determined. This should make it possible, for instance, to distinguish between a three-dimensional island growth and a more two-dimensional layer-by-layer growth. With this in mind, we will use the single ^{57}Fe probe layer method for an investigation of the central region of the iron multilayer and the bottom (^{57}Fe on Ag) interface. The results can be combined with those previously obtained for the top (Ag on ^{57}Fe) interface[6] for an investigation of the growth of the entire Fe multilayer.

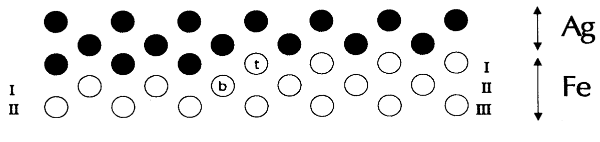

FIG. 1. Five different iron positions I, I_t, I_b, II, and III close to a terraced Fe/Ag(100) interface.

II. EXPERIMENT

For the present CEMS study three samples have been prepared. Sample 1, Ag/(1.4^{57}Fe/5.4Fe/10Ag)$_1$/9Au; sample 2, Ag/(3Fe/1^{57}Fe/3Fe/10Ag)$_3$/9Au; sample 3, Ag/(4.7Fe/1^{57}Fe/4Fe/10Ag)$_1$/9Au.

The epitaxial growths were carried out in a PHI-400 MBE machine equipped for RHEED and Auger-electron spectroscopy. The good lateral match between the bcc Fe(001) and fcc Ag(001) lattices in the planes is not found for the vertical direction. The difference in the vertical stacking between the fcc and bcc lattices result in a large vertical mismatch of about 16%. The growth of the bcc Fe(001) and fcc Ag(001) templates with a high density of atomic steps is strongly affected by this large atomic vertical mismatch. In order to obtain good growth one has to use Ag(001) substrates for which the atomic terraces are significantly larger than the average Fe(001) nucleation site separation. Substrates with atomic terraces of several tens of nm are required to grow good ultrathin epitaxial Fe(001). The preparation of Ag(001) substrates is rather difficult. Ag single crystals are very soft and a Ag(001) substrate which has undergone mechanical polishing exhibits a badly damaged surface region. We found that it is necessary to remove a layer several μm thick by means of a proper electropolishing procedure before the substrate is subjected to a UHV annealing and sputtering treatment. After the treatment the average terrace size is several hundred nm.[7]

Figure 2 shows the RHEED oscillations as a function of time during the growth of Fe(001) on a Ag(001) single-crystal substrate at 295 K. The RHEED intensity was measured at the RHEED specular spot, the angle of incidence of electron beam was ~1.3° which corresponds to the first anti-Bragg condition. The RHEED patterns and the RHEED specular spot intensity oscillations indicate that at least 3–4 ML of Fe have to be deposited in order to heal the distortions produced by the mismatch in

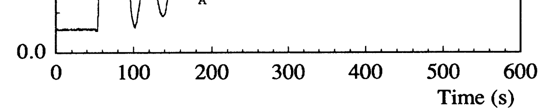

FIG. 2. Reflection high-energy electron-diffraction intensity oscillations as a function of time during the growth of Fe(001) on a single-crystal substrate of Ag(001) at 295 K. The growth of the ^{57}Fe layer in sample 2 was terminated at the fourth minimum (point *A*) and that in sample 3 was terminated at the sixth maximum (point *B*). The thickness of samples 1, 2, and 3 was determined by dividing the growth time by the stationary period of the oscillations.

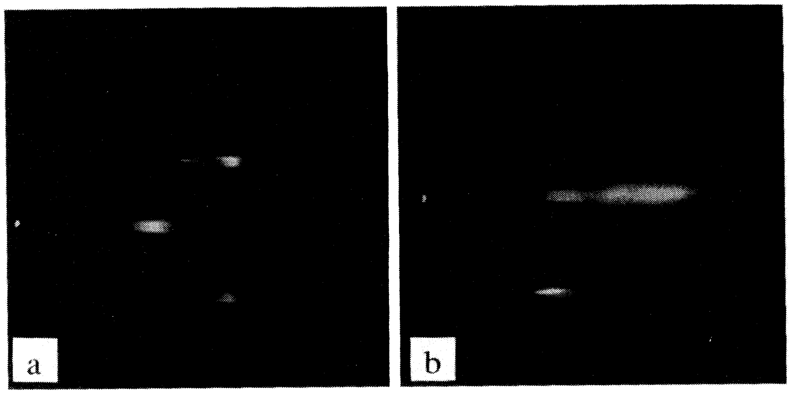

FIG. 3. Reflection high-energy electron-diffraction patterns for a 5.7-ML-thick Fe(001) layer grown on a Ag(001) single-crystal substrate at room temperature: (a) along a {100} azimuth, (b) along a {110} azimuth. Note that the RHEED streaks are split. The inverse value of the observed RHEED splitting suggests that an average minimum separation between islands exist of ~6 nm.

the atomic steps. After 5–6 atomic layers of Fe(001), a constant periodicity in the RHEED intensity oscillations is observed. The Fe growth on Fe(001), Cr(001), and Ag(001) templates at room temperature exhibits a well-defined splitting in the RHEED streaks (Fig. 3), that represent a characteristic lateral spacing. It can be shown by a computer simulation that the reciprocal of the RHEED streak splitting is proportional to the average spacing between atomic islands. This suggests that for the present samples the average separation between atomic terraces is about 5–6 nm for RT growth.[8] This conclusion was confirmed by the recent STM studies of the growth of Fe on Fe(001) whiskers.[9]

Mössbauer spectra were collected over periods of weeks using CEMS. The stability of the Mössbauer parameters over those measuring times was as follows: Δi.s.$=0.001$ mm/s, ΔQS$=0.003$ mm/s, and $\Delta H_{\rm hf}=1$ kOe.

For the investigation of the growth of the Fe multilayer in Fe/Ag structures the results for the samples above will be combined with those obtained for the samples studied previously:[6] Sample 4, Ag/(5.7Fe/1^{57}Fe/10Ag)$_3$/9Au; sample 5, Ag/(8.2Fe/1^{57}Fe/10Ag)$_1$/9Au. Sample 4 was grown at room temperature and the top three Fe layers of sample 5 were grown at ~420 K.

III. RESULTS

The Mössbauer spectra for samples 1, 2, and 3 are presented in Fig. 4. For sample 1 and 2 the asymmetry in the line intensities and the asymmetric shape of lines one and two clearly indicate the presence of several sextets in the spectra. For an analysis of these spectra, we need to associate these different components with the various Fe sites in the multilayer structure. This can be done based on an analysis of the i.s., QS, and $H_{\rm hf}$ values.

Self-consistent spin-polarized local-spin-density calculations have been performed for the case of a thin Fe(001) film with an Ag overlayer.[2] The Fe surface is flat, i.e., no terraces are present. The calculations give values for the charge densities in the Fe film that are related to i.s. values, and give values for the spin densities in the ground state from which $H_{\rm hf}(0)$ can be determined. Since our measurements were performed at room temperature, the analysis of $H_{\rm hf}$ values is not very important for the interpretation of the spectra. The charge-density values indicate that the i.s. at the Fe/Ag interface is expected to be larger than that for bulk iron. For ^{57}Fe atoms that do not make contact with Ag atoms the calculations show almost the same value of i.s. as in bulk iron. This result is also predicted by the theory of Miedema and Van der Woude for the concentration dependence of i.s. values in binary Fe$_c$X$_{1-c}$ alloys.[10] According to this theory the alloying process causes a chemical and a physical contribution to the i.s. The chemical contributions are (a) an interatomic electron transfer to the more electron negative element and (b) an intra-atomic *s*-*d* transfer. The physical contribution is a volume adjustment if the atomic volume of the two constitutes are different. The concentration dependence of the i.s. can then be described by the proportionally relationship i.s. (:) C_xIS$^{\rm max}$, where i.s.$^{\rm max}$ is the value for the i.s. of a ^{57}Fe nucleus completely surrounded by the X atoms. C_x represents the contact surface concentration, defined as $C_x=(1-c)V_x^{2/3}/[cV_{\rm Fe}^{2/3}+(1-c)V_x^{2/3}]$, where V_x and $V_{\rm Fe}$ stand for the molar volumes of X atoms and Fe atoms, respectively.

The experimental values for i.s. in disordered Fe$_{1-c}$Ag$_c$ alloys increase monotonically with the Ag concentration up to a maximum average value of IS$^{\rm max}=0.50$ mm/s for Fe atoms implanted in silver (Fig. 5).[11–13] This result confirms the relationship between i.s. and the Ag concentration as expected from the theory. For MBE-grown Ag(100)/Fe/Ag structures, the growth takes place on a terraced surface. Various Fe sites with different (Fe,Ag) NN configurations are schematically indicated in Fig. 1. Fe site I$_b$ has five NN Fe and three NN Ag atoms, Fe site I has four NN Fe and four NN Ag atoms, Fe site I$_t$ has three NN Fe and six NN Ag atoms. Fe sites II, III, etc. have no NN Ag atoms. Since the isomer shift is expected to decrease with a decrease in the contact surface concentration of the Ag atoms, these sites can be associated now with components in the Mössbauer spectra. This was illustrated by the results obtained from sample 4 and 5, where a value i.s. = 0.21 mm/s associated with Fe site I is in very good agreement with the i.s. values found in disordered Fe$_{1-c}$Ag$_c$ alloys for $c=0.5$ (Fig. 5). For ^{57}Fe atoms at sites that are one or more layers removed from the Fe/Ag interface, we expect the i.s. values to be close to zero.[2] These expectations were confirmed by the values i.s. ≤ 0.06 mm/s found for ^{57}Fe at sites II and III in samples 4 and 5.[6]

The distinction between Fe sites I and the other sites that do not make contact with Ag atoms at the interface was further supported by the QS values measured in previous MES studies.[4–6] The larger size of the Ag atoms will destroy the cubic symmetry for the iron atoms at the Fe/Ag boundaries.[14] For instance, for site I, one would expect a tetragonal distortion that produces an electric field gradient at the ^{57}Fe nucleus. This was confirmed by a value QS$=-0.10$ mm/s for Fe sites I, whereas much smaller values of less than QS$=-0.03$ mm/s were found for Fe sites II and III.[4–6]

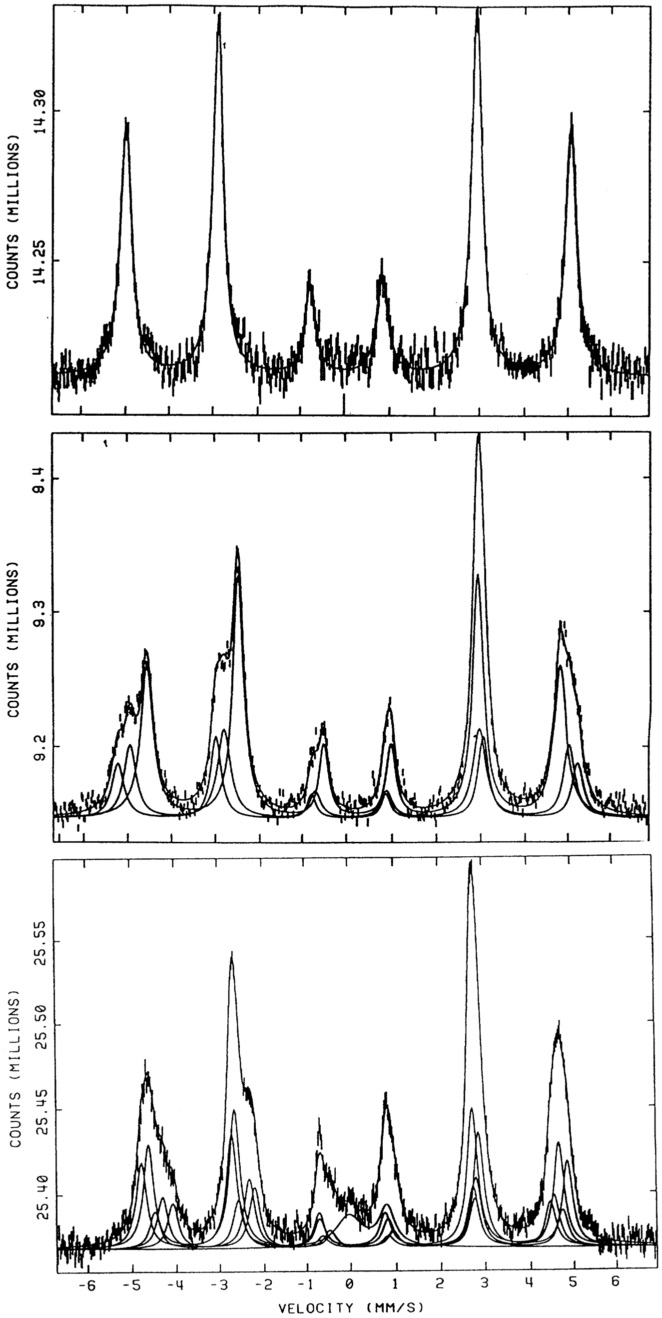

FIG. 4. Conversion electron Mössbauer spectroscopy spectra of MBE-grown Ag/(4.7Fe/1^{57}Fe/4Fe/10Ag)/9Au (top), Ag/(3Fe/1^{57}Fe/3Fe/10Ag)$_3$/9Au (center), and Ag/(1.4^{57}Fe/5.4Fe/10Ag)/9Au (bottom).

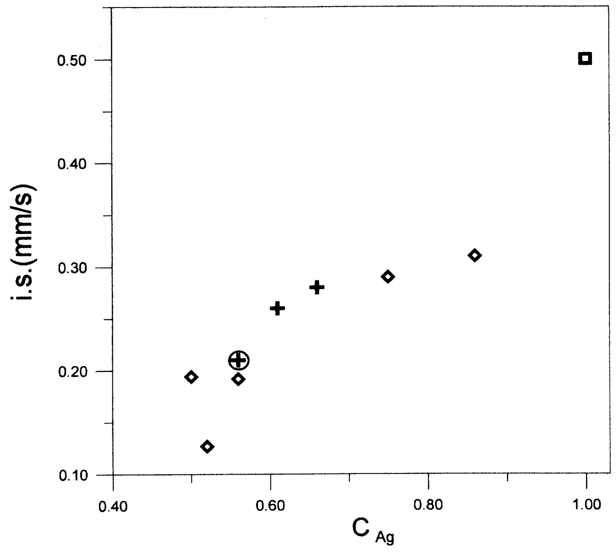

FIG. 5. Average isomer shift versus contact surface concentration for disordered Fe$_{1-c}$Ag$_c$ alloys (◇ Ref. 11, + Ref. 12, □ Ref. 13) and for the Fe site I measured in samples 4 and 5 (○) (Ref. 6).

Fe sites I$_t$ and I$_b$ are located at the edge of terraces. They can be associated with components in the Mossbauer spectra based on their i.s. and QS values and on relative area considerations.[6] For a one step terrace the intensities of these two components should be the same.

Based on this discussion of the expected i.s. and QS values, we have analyzed the results of the least-square fits of the spectra shown in Fig. 4. The results are presented in Table I. The spectrum obtained for sample 2 has been fitted with three sextets. The i.s. and QS values of components 2 and 3 are very close to zero as expected for Fe sites with no Ag nearest neighbors, i.e., Fe sites II and III. Ohnishi, Weinert, and Freeman[2] calculated for a Ag/5Fe/Ag(001) structure that the value of $H_{\rm hf}(0)$ for Fe sites III is larger than for sites II. For previous temperature-dependent MES measurements,[1,4,5] we estimate that the temperature dependence for the two sites is not much different. Based on these considerations, we conclude that components 2 and 3 are most likely associated with sites II and III, respectively. The i.s. and QS values and the large line width of sextet 1 show that this component is associated with a distribution of Fe sites at the Fe/Ag interface that have different (Fe,Ag) NN configurations. The distribution may correspond to Fe sites I, I$_t$, and I$_b$ at the Fe/Ag interface. Due to the small intensity of component 1 in the spectrum for this sample, we did not attempt to distinguish between these sites in the fit.

The spectrum of sample 1 has been fitted with five sextets and one doublet. Based on the same analysis as for sample 2, we conclude that sextets 4 and 5 correspond to Fe sites II and III, respectively. Sextets 1, 2, and 3 are as-

TABLE I. Values of the magnetic hyperfine fields H_{hf}, the quadrupole splittings (QS) 2ϵ, and the isomer shifts (i.s.) measured with respect to natural iron.

		Sample 1: Ag/(1.4^{57}Fe/5.4Fe/10Ag)/9Au			
Component	Rel. Area	H_{hf} (kOe)	i.s. (mm/s)	QS (mm/s)	Γ (mm/s)
1	0.11	287	0.11	0.03	0.29
2	0.15	276	0.19	−0.12	0.29
3	0.13	266	0.23	−0.07	0.29
4	0.30	289	0.02	−0.01	0.29
5	0.24	300	0.05	−0.03	0.29
6	0.07		0.38	0.41	0.60
		Sample 2: Ag/(3Fe/1^{57}Fe/3Fe/10Ag)$_3$/9Au			
Component	Rel. Area	H_{hf} (kOe)	i.s. (mm/s)	QS (mm/s)	Γ (mm/s)
1	0.23	271	0.15	−0.10	0.42
2	0.40	284	0.04	0.01	0.27
3	0.37	294	0.03	0.00	0.27
		Sample 3: Ag/(4.7Fe/1^{57}Fe/4Fe/10Ag)/9Au			
Component	Rel. Area	H_{hf} (kOe)	i.s. (mm/s)	QS (mm/s)	Γ (mm/s)
1	1.00	313	0.02	−0.01	0.30

sociated with Fe sites at the Fe/Ag interface. Here, Fe site I_t has a (5Fe, 3Ag), Fe site I has a (4Fe, 4Ag), and Fe site I_b has a (3Fe, 6Ag) NN configuration. Since the i.s. values increase with an increase in the surface concentration of Ag NN, this indicates that components 1, 2, and 3 correspond to Fe sites I_t, I, and I_b, respectively.

The i.s. and QS values of the doublet component 6 in the spectrum of sample 1 can be compared with those obtained in disordered Fe_cAg_{1-c} alloys.[11] At 300 K these alloys are paramagnetic for $x \leq 0.3$ and the average values of i.s. and QS increase with decreasing values of c. Extrapolation to $c \approx 0$ would give values that are in agreement with the i.s. and QS values of component 6 of sample 1. Taking the large linewidth of this component into account, we conclude that the doublet in the spectrum for sample 1 is associated with ^{57}Fe atom that have zero or one Fe NN.

The results obtained for sample 3 clearly prove that the value of i.s. is close to zero for Fe atoms with no Ag nearest neighbors. The ^{57}Fe atoms deposited in the fifth and sixth ML of a 9.7-ML iron layer produce a simple symmetric Mössbauer spectrum that can be well fitted with only one sextet (Fig. 4). The linewidth of the outside lines is $\Gamma = 0.30$ mm/s. This is only slightly larger than the value $\Gamma = 0.27$ mm/s obtained for the iron calibration spectrum. Most of the line broadening can be explained from the distribution of MES parameters due to the 0.02% abundance of ^{57}Fe in the natural iron of the nonprobed layers and the spread of ^{57}Fe atoms over two Fe layers. The narrow linewidth of the spectrum shows that the value of H_{hf} does not change much in the central region of the Fe film. This is in accordance with the MES study of Liu and Gradmann.[5] The i.s. = 0.02 mm/s and QS = −0.01 mm/s obtained for the spectrum of sample 3 confirm that for a Fe site with no Ag NN the i.s. and QS values are much smaller than for Fe sites I, I_b, and I_t. It may be noted that at the center of a 9.7-ML Fe film that is sandwiched between two Ag layers, the electron density at the ^{57}Fe nucleus is still slightly smaller than that in bulk iron.

IV. DISCUSSION

We have investigated a number of MBE-grown samples where a ^{57}Fe atomic layer was deposited as a probe layer at various locations in the Fe multilayer of Fe/Ag(100) structures. After the analysis of the MES results in the previous section, we have obtained the distribution of ^{57}Fe atoms over the various Fe sites I, II, III, etc., i.e., in the different atomic layers of the Fe/Ag structures. This makes it possible to discuss the MES results of each sample for a better understanding of the growth of Fe on the Ag(001) substrate.

MES study of the lower Ag(100) substrate/Fe interface

Sample 1: Ag/(1.4^{57}Fe/5.7Fe/10Ag)/9Au. The areas of the components shown in Table I represent the distribution of ^{57}Fe atoms over the various Fe sites close to the Fe/Ag interface for the first 1.4 ML equivalent of deposited ^{57}Fe. The areas show that 21%, 18%, and 15% of the first ML above the Ag substrate is in the form of ^{57}Fe atoms in sites I, I_b, and I_t, respectively. Two conclusions can be drawn from this information. First, the relative areas corresponding to I_t and I_b sites for the lower and upper Fe/Ag boundary are similar. This indicates that, also, the atomic step densities in the two regions are similar. Second, the first 1.4 ML equivalent of the deposited Fe does not form a smooth layer on the Ag substrate. After a deposition of 1.4 ML of iron 46% of the substrate is not covered by Fe. This indicates that the initial growth on the Ag surface is a three-dimensional (3D) island growth.

The doublet in the spectrum shows that 7% of the ^{57}Fe atoms that enter the substrate replace bulk Ag atoms that then become part of the interface. This mechanism is observed by other techniques in other systems[15,16] and is usually referred to as interface atom exchange. The evidence for interface exchange between the Ag substrate and the added Fe atoms was also recently presented by Egelhoff.[14] These Fe atoms that are part of the Ag substrate are nonmagnetic and are responsible for the quadrupole-split doublet in the spectrum for this sample.

Adding the ^{57}Fe atoms exchanged at the interface and the ^{57}Fe located at sites I, I_b, and I_t, we conclude that a total of 0.64-ML equivalent of ^{57}Fe makes contact with the Ag at the interface. The remaining 0.76 ML of ^{57}Fe atoms are not in direct contact with the Ag. These atoms are most likely located at sites II and III. The narrow linewidths and the small i.s. and QS values for components 2 and 3 for this sample (Table I) suggest strongly that the substrate Ag atoms are not appreciably intermixed with the Fe atoms in the second and third layer above the Ag substrate. If the interface exchange between Fe and Ag atoms had resulted in an appreciable presence of the Ag atoms in the second and third Fe layer then the linewidths for the components associated with sites II and III would have been noticeable wider, mainly because the presence of Ag in these atomic layers will produce an i.s. distribution in the MES results.

The equivalent of 0.76 ML of ^{57}Fe located in the second and third atomic Fe layers can be explained by a significant multilayer formation, at least 3 ML thick during the initial stages of growth. Alternatively, this result could be obtained if the interface ^{57}Fe atoms are exchanged for ^{56}Fe atoms that are deposited in subsequent stages after the deposition of ^{57}Fe has stopped.

MES study of the inner Fe atomic layers

Sample 2: Ag/(3Fe/1^{57}Fe/3Fe/10Ag)$_3$/9Au. The MES results obtained for this sample show that deposition of an equivalent of 3 ML of natural Fe is not sufficient to cover all areas of the Ag substrate. 23% of the ^{57}Fe atoms show MES parameters that are consistent with the presence of these atoms in sites I and I_t. A partial coverage of the substrate after deposition of an equivalent amount of 3 ML is not surprising. The RHEED patterns and RHEED intensity oscillations show a very irregular behavior especially during the growth of the first 3 ML of Fe (Fig. 2).[7] The RHEED patterns exhibit a strong diffuse background that oscillates in intensity and the RHEED oscillation periods are very irregular.

Sample 3: Ag/(4.7Fe/1^{57}Fe/4Fe/10Ag)/9Au. The ^{57}Fe atoms deposited in the fifth and sixth ML of a 9.7-ML-thick Fe layer produce a simple symmetric Mossbauer spectrum that can be well fitted with only one sextet (Fig. 4). It is very unlikely that some of this ^{57}Fe is present in the third or lower Fe layer because the value of $H_{\mathrm{hf}} = -327$ kOe for site III in the spectrum for sample 5 (Ref. 6) is significantly larger than that found for sample 3. The presence of ^{57}Fe in the third Fe ML would result in a much larger line broadening than was observed. Based on these considerations, we conclude that the MES results show that most of the ^{57}Fe is present in the fifth and sixth atomic layer above the Ag substrate as intended. This result is different from that of the previous two samples where the ^{57}Fe was present in at least three Fe layers due to atomic exchange and multilayer formation. The sudden change in behavior shows that 5 ML of Fe(001) represents a critical thickness for the formation of smooth, homogeneous Fe(001) films.

This last conclusion based on the MES results of sample 1, 2, and 3 is in excellent agreement with the growth behavior deduced from the observation of RHEED patterns and RHEED intensity oscillations. The deposition of an equivalent of 3 ML of Fe(001) was required to substantially reduce a diffuse background signal in the RHEED patterns and 5–6 ML of Fe was required in order to obtain RHEED oscillations that are characterized by a stationary period that corresponds to the deposition of one atomic layer (Fig. 2).[7]

MES study of the upper Fe/Ag(100) interface

Sample 4: Ag/(5.7Fe/1^{57}Fe/10Ag)$_3$/9Au. The results of a MES study of this sample were presented in a recent paper.[6] Here, we will summarize only the information that is of interest to the subject of the present paper. The presence of ^{57}Fe atoms in I, I_b, and I_t sites was 38%, 21%, and 21%, respectively. 19% of the ^{57}Fe atoms do not make contact with Ag atoms at the upper Fe/Ag interface. Considering the 2% abundance of ^{57}Fe in natural Fe in the nonprobed layers, we estimate that about 90% of the ^{57}Fe in the probe layer is in contact with the Fe/Ag and 10% of it is present in Fe sites II and possibly III. This result is quite different from that obtained for sample 1 where the probe layer was grown on top of the Ag substrate. Here only 54% of the Ag substrate was covered by ^{57}Fe even though 1.4 ML of ^{57}Fe was used.

The growth of the top Fe layer confirms the previous result obtained for the growth of the fifth and sixth Fe ML. That is, the growth of films thicker than 5 ML proceeds in a quasi-layer-by-layer mode in which partial coverage is limited mostly to the top two atomic layers. This is in agreement with the interpretation of RHEED results[7] and is also consistent with the observation by scanning tunneling microscopy (STM). Recently, Stroscio, Pierce, and Dragoset[9] quoted from the STM technique a value of 0.11 nm for the rms surface roughness for a RT growth of Fe(001) on Fe(001) whisker facets. This rms value indicates a surface that consists mainly of three atomic layers. The iron on iron growth at RT for the STM study was very similar to the RT growth observed for Fe(001) on Ag(001). These two systems exhibited very similar RHEED patterns, although the intensity of the RHEED oscillations decayed more rapidly for the RT growth of Fe(001) on an iron whisker than for the growth of Fe(001) on Ag(001).

The existence of the Fe sites I_b and I_t shows the presence of Fe terraces at the Fe/Ag(100) interface. The mean distance between the atomic terraces can be estimated from the relative intensities of the components that are associated with sites I, I_t, and I_b. In a previous paper, we estimated the average terrace size by assuming that only one atomic layer is unfilled during the growth.[17] Here, we will use a model that is more in accordance with the quasi-layer-by-layer growth that, as we have seen, applies to the top of the Fe multilayer. We assume that after deposition of 5.7 ML, five Fe layers are completely filled, the sixth Fe layer is half filled with $N \times N$ as the average number of atoms per terrace and additional atoms ($N_1 \times N_1$) equivalent to 0.2 ML sit on top of the sixth Fe layer (Fig. 6). It follows from $N_1^2/N^2=0.2$ that $N_1=0.63N$. The ratio $(\mathrm{I}_t+\mathrm{I}_b)/\mathrm{I}$ of Fe atoms located at the edges and those present on the terraces at least one atomic distance removed from the edge, is given by $R=[8(N-1)+4(N_1-1)+4N_1]/[(N^2-8N+8)-(N_1+1)^2+(N_1^2-4N_1+4]$. From the experimental value $R=1.1$, we calculate $N=11$. The corresponding mean distance L between equivalent atomic terraces can be expected to be between $\sqrt{2}Na$ and $2Na$, where $a=0.28$ nm for Fe(100). This gives a value of L between 4.3 and 6.2 nm.

The growth of Fe on a Ag(001) substrate exhibits a well-defined RHEED streak splitting after the first 5 Fe ML have been deposited. The reciprocal value of the RHEED streak splitting (Fig. 3) allows one to estimate a mean distance of 5–6 nm between terraces.[8] The two values obtained from the different techniques are in good agreement with each other.

The use of the I_t and I_b areas for a determination of the average terrace size of the Ag substrate is more difficult. The fact that 7% of the deposited Fe atoms enter the substrate replacing the Ag atoms indicates the formation of additional Ag atomic steps. This suggests that the one step terrace model may not be a proper model for the lower Ag/Fe interface. Nevertheless, since the values of relative areas for I_t and I_b sites are similar for the upper and lower Ag/Fe boundaries, we can conclude that the atomic step densities for the two areas are similar, i.e., the terrace size on the Ag substrate that was several 100 nm has been reduced by at least a factor 10 due to the deposition of Fe atomic layers.

The presence of site II atoms in quasi-layer-by-layer growth is not surprising. The template on which ^{57}Fe is deposited is not atomically flat. This is illustrated in Fig. 6 where the top of the first 5.7-ML Fe layers is shown on which the ^{57}Fe is deposited. The ^{57}Fe atoms that are deposited in the lowest unfilled atomic layer have a good chance to be converted by additional incoming ^{57}Fe atoms. This creates then site II atoms.

Sample 5: Ag/(8.2Fe/1^{57}Fe/10Ag)/9Au. In this sample the last three atomic layers were grown at a raised temperature, $T_{\mathrm{sub}} \sim 420$ K. The sample exhibits much larger atomic terraces than those grown at RT.[8] The density of atomic steps decreases significantly and, consequently, the measured intensities in the Mossbauer spectrum components that correspond to sites I_b and I_t ought to be significantly weaker. In fact, a visual inspection of the spectrum of sample 5 showed that the site I component in the spectrum is resolved from the site II and III components and the spectrum can be fitted well by only taking into account site I, II, and III ^{57}Fe atoms.[6] The intensity of site I_t and I_b components is too small to be included in the fit. This observation gives strong support for the identification of the components in the previous samples.

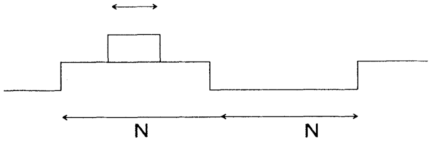

FIG. 6. Schematic representation of a mean sized terraced surface of $N \times N$ atoms with additional atoms $N_1 \times N_1$ on top.

The relative intensity for site I, II, and III Fe atoms in sample 5 is 0.58, 0.28, and 0.14, respectively. As in the previous sample, the presence of sites II and III atoms can be partially explained by the 0.2% abundance of ^{57}Fe in the natural iron of the unprobed layers and by the growth on two atomic Fe layers that leads to partial coverage of ^{57}Fe by additional incoming ^{57}Fe atoms. However, the concentration of ^{57}Fe at sites II and III in the sample prepared at 420 K is at least twice that of the sample prepared at RT. This suggests that exchange diffusion between ^{57}Fe and ^{56}Fe occurs if the sample is grown at 420 K.

V. CONCLUSION

A Mössbauer-effect-spectroscopy study of the iron multilayer in molecular-beam-epitaxy grown Fe(001)/Ag(001) structures has been performed by using one monolayer of ^{57}Fe as a probe layer. Different Fe sites with different nearest-neighbor (Fe,Ag) configurations in the multilayer can, in principle, be recognized in the Mossbauer spectrum from the differences in MES parameters. This makes it possible to determine the concentration of ^{57}Fe atoms in the different Fe layers and, thus, get information about the growth process at different location in the Fe multilayer.

The results show that the growth of the Fe layers in the lower part of the Fe multilayer is quite different from the growth in the upper part of the multilayer. After deposition of the 1.4-ML equivalent of ^{57}Fe on the Ag substrate, only 54% of the substrate is covered by ^{57}Fe atoms. The equivalent of 0.76 ML of ^{57}Fe is located in a Fe multilayer formation that is at least one atomic layer removed from the Ag substrate. Even after deposition of the equivalent 3 ML of Fe, 23% of the substrate is still not covered by Fe atoms. This result clearly shows that initially 3D islands are grown on the Ag substrate. Furthermore, as indicated by the large areas of the I_t and I_b components, the deposition of Fe produces an intermixing of Fe and Ag atoms. This increases significantly the atomic step density at the lower Ag/Fe boundary. The observation that 7% of the incoming ^{57}Fe takes part in interface atom exchange with the substrate Ag atoms is also evidence of intermixing. The atom exchange mechanism is absent when the Ag atoms are deposited over the Fe template at the upper Fe/Ag interface.

The deposition of Fe atoms on an Ag substrate is an example of the growth of a high-surface-free-energy metal on top of a low-surface-free-energy substrate.[18] Furthermore, the mismatch in the Fe and Ag lattices produces strain energy. Both the surface-free-energy balance and the presence of strain energy can explain how the mechanisms of 3D island growth and intermixing of overlayer and substrate, observed during the initial growth, can be used to lower the total free energy.

After deposition of 4.7 Fe ML the Fe film starts to grow in the quasi-layer-by-layer mode. This represents a critical thickness for the formation of smooth Fe(001) films and from there on partial coverage of atomic surfaces is mostly limited to the top two atomic layers.

In contrast with the bottom Fe/Ag boundary, the top Fe/Ag interface is very sharp with 90% of the deposited 1-ML ^{57}Fe actually making contact with the Ag at the top Fe/Ag interface. Interface atomic exchange between Fe and Ag atoms is not observed at the upper Fe/Ag boundary for a sample grown at RT. However, the MES results indicate that for Fe layers deposited at ~420-K atomic exchange between ^{56}Fe and ^{57}Fe takes place.

A comparison between MES and diffraction techniques such as RHEED shows that MES confirms the interpretation of RHEED measurements for the upper region of the Fe multilayer. Both techniques also give the same estimate for the average terrace size. However, MES has the advantage in giving more quantitative information for the initial deposition of Fe on the Ag substrate. Mössbauer-effect spectroscopy can determine the amount of coverage of the substrate and the relative amount of atoms that participate in the exchange diffusion process at the Ag/Fe interface. Furthermore, whereas the diffraction techniques can only give information about the surface condition of the sample while it is growing or after the growth has been completed, MES can provide information about the final configuration of deposited Fe atoms at different locations in the completed sample.

The difference in growth modes for the upper and lower parts of the Fe film can explain some surprising results presented in previous MES studies. Keavney *et al.* have studied $[\mathrm{Fe}_9(100)/\mathrm{Ag}_{40}(100)]_{25}$ multilayers by using a 2-ML ^{57}Fe probe layer.[4] From the difference in MES parameters they conclude that the Fe sites at the top and bottom Fe/Ag interface are different. However, because a 2-ML probe layer was used, the MES parameters presented in that study were averaged over many sites. Our study shows that due to different growth modes, the distribution of ^{57}Fe atoms in the vicinity of the upper and lower Fe/Ag boundaries is quite different. This difference in distributions explains the difference in averages MES parameters for upper and lower interface. Indeed, an inspection of the data presented in Table I and that previously presented[6] shows that the MES parameters averaged for 2 ML of ^{57}Fe at the upper and the lower interface should give smaller values of i.s. and QS but larger values of H_{hf} at the lower Fe/Ag interface as was observed by Keavney *et al.*[4]

For site II Fe atoms close to the upper and lower Fe/Ag interface, the magnetic hyperfine fields are very similar: $H_{\mathrm{hf}} = -292$ kOe at the top and $H_{\mathrm{hf}} = -289$ kOe at the bottom. On the other hand, for Fe sites I, the value of $H_{\mathrm{hf}} = -276$ kOe at the lower interface is significantly different from the value of $H_{\mathrm{hf}} = -267$ kOe at the upper interface. Also, the absolute H_{hf} values for the I_t and I_b sites are 10 kOe larger at the lower than at the upper Fe/Ag interface. It is unlikely that this difference is due to Fe sites I being different at the upper and bottom interface, because the i.s. and QS values are the same for the two locations.

We propose that the difference in H_{hf} for top and bottom Fe/Ag boundary may be related to the presence of Ruderman-Kittel-Kasuya-Yosida-like spin-density oscillations that couple ferromagnetic multilayers across a nonmagnetic metal spacer such as Ag.[19–21] A contribution from the *s*-spin-density oscillation to H_{hf} is expected to be present at the top Fe/Ag interface if the overlaying Ag film in turn is covered by another Fe multilayer as is the case for sample 4. Depending on the phase of the oscillation, the *s*-spin-density would either add or subtract from the value of H_{hf} at the top Fe/Ag interface. The contribution to the value of H_{hf} at the bottom interface would be much smaller than at the top. Support for this explanation is provided by a sample where only one multilayer of Fe is present: Ag/5.7Fe/1^{57}Fe10Ag/9Au.[6] Consequently, no contribution from a spin-density oscillation through the overlying Ag is present here. Unfortunately, the statistics in the spectrum for this sample are not good enough for a fit with as many components as the spectrum of sample 4. By fitting the spectrum for Ag/5.7Fe/1^{57}Fe/10Ag/9Au with only two sextets, we obtained a value $H_{\mathrm{hf}} = -275$ kOe averaged over Fe sites I, I_t, I_b. This is in excellent agreement with the average $H_{\mathrm{hf}} = -276$ kOe for these sites at the bottom interface in sample 1. An identical two sextet fit for sample 4 gives an average of $H_{\mathrm{hf}} = -267$ kOe. This result suggests that the *s*-spin-density oscillation through the Ag has a net value along the direction of the magnetic moments of Fe site I iron atoms, contributing about +9 kOe to the value of H_{hf} of iron atoms at these locations.

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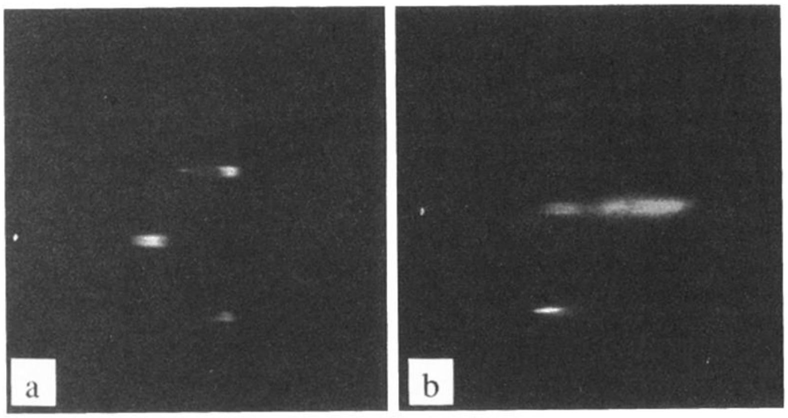

FIG. 3. Reflection high-energy electron-diffraction patterns for a 5.7-ML-thick Fe(001) layer grown on a Ag(001) single-crystal substrate at room temperature: (a) along a {100} azimuth, (b) along a {110} azimuth. Note that the RHEED streaks are split. The inverse value of the observed RHEED splitting suggests that an average minimum separation between islands exist of ~6 nm.