

Mössbauer-effect investigation of the Fe(001)/Ag(001) interface

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The Fe(001)/Ag(001) interface in molecular-beam-epitaxy-grown (001) structures has been investigated using conversion electron Mössbauer spectroscopy. One monolayer of ^{57}Fe is used as a probe layer. The Mössbauer-effect study shows that the Fe/Ag interface consists of atomic terraces, one atomic layer in height. Three Fe sites can be distinguished at the Fe/Ag interface. The average size of the terraces can be determined from the relative intensity of the three components in the Mössbauer spectrum. By growing the sample at 420 K the terrace size can be increased significantly. However, at this temperature, diffusion of the ^{57}Fe into the underlying Fe layers becomes important.

I. INTRODUCTION

Metallic artificial structures such as overlayers, trilayered sandwiches, and modulated structures can be prepared by using the molecular-beam-epitaxy (MBE) technique. This method has opened a new field for studying fundamental properties of metals and also for the applications of these properties. Mössbauer-effect spectroscopy (MES) is an important technique for investigating the new materials produced because in principle it can probe the new structures with an atomic scale resolution. Spin-density and charge-density calculations¹ show the MES parameters such as the isomer shift (i.s.) and the magnetic hyperfine field H_{hf} should depend on the location of the ^{57}Fe atoms with respect to the interfaces in the structure. As a consequence, the use of natural iron for one of the multilayers in the structure is of limited use for detailed studies of these materials. MES for such materials would sample the whole distribution of values for the isomer shifts, quadrupole shifts (QS), and magnetic hyperfine fields H_{hf} throughout the iron multilayer. This may result in a complicated spectrum where the components from different layers cannot be resolved. A better way of obtaining information is by using a layer of almost pure ^{57}Fe as a probe layer. By varying the position of this probe layer, the information about charge density and spin density can be obtained for locations throughout the multilayer. It is best to use a probe layer of ^{57}Fe only one atomic layer thick. Even then, the ^{57}Fe may be distributed in two or more atomic layers, due to the roughness of the surface on which subsequent layers are deposited. Samples grown with many superlattice periods may have a wider distribution of MES parameters than samples with only one period because the quality of the interface decreases with the growth of more periods. This would cause line broadening in the Mössbauer spectrum.

We have prepared the structure Ag/5.7 Fe/ ^{57}Fe /10Ag mainly for a detailed investigation of the

Fe/Ag interface. The structure has been made with ^{57}Fe probe layers only one monolayer (ML) thick. Samples with one and three periods were prepared in order to see the effect of multiperiod structures on the resolution in the Mössbauer spectrum.

II. EXPERIMENT

The preparation of Ag(001) substrates has been described in previous papers.² Here we will summarize only those aspects and ideas which are relevant to the experiments discussed in this paper. The experiments were carried out in a PHI-400 MBE machine equipped with reflection high-energy electron diffraction (RHEED) and Auger electron spectroscopy. The RHEED studies showed that the Fe growth on Ag(001) at room temperature proceeds in a quasi-layer-by-layer growth in which the surface roughness is confined mostly to the last two atomic layers.³ The Fe growths on Fe(001) and Ag(001) templates at room temperature exhibit a well-defined splitting in the RHEED streaks. The shape of the observed streak splitting is characteristic of the intersection of Ewald's sphere with reciprocal rods consisting of alternating segments of hollow cylinders and straight lines. This behavior is caused by formation of clusters of atoms in one-atom-high islands with a strong correlation of the distances of separation of the island centers. The RHEED streak splittings 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 (terraces). The inverse value of the observed RHEED splitting suggests that an average minimum separation between atomic islands is $\sim 5\text{--}6$ nm for RT growth. The good lateral match between the Fe(001) and Ag(001) lattices in the plane is not found for the vertical direction. The difference in the vertical stacking between the fcc and bcc lattices results in a large vertical mismatch of approximately 16%. The growth of bcc Fe(001) on fcc Ag(001) templates with a high density of atomic steps is

strongly affected by this large atomic vertical mismatch. In order to maintain good growth, one has to use Ag(001) substrates characterized by atomic terraces which are significantly larger than the average Fe(001) nucleation site separation. Substrates with atomic terraces of several tens of nanometers are required to grow good ultrathin epitaxial Fe(001). In all our growths the first few atomic layers of Fe(001) are affected by Ag(001) substrate atomic steps. At least 3–4 ML of Fe have to be deposited in order to heal the distortions produced by the mismatch at the atomic steps. After five to six atomic layers of Fe(001), a constant periodicity in the RHEED intensity oscillations is achieved. The surface of the first Fe layer grown at room temperature does not change sufficiently upon annealing to produce any observable changes in the RHEED patterns. RHEED streak splitting remains unchanged even at 510 K. The Ag Auger peak intensity measurements indicate that no appreciable interdiffusion between the Ag(001) substrate and a 6-ML-thick Fe layer occurs up to 470 K. However, the RHEED patterns change significantly when the growth is carried out at raised temperatures. In our sample-preparation procedure, the first 5–6 ML of Fe were grown at RT to protect the Ag-Fe interface from atomic intermixing. Then the substrate temperature was raised and three to four additional atomic layers of Fe were added. The growth at raised substrate temperatures exhibited a behavior which was similar to that observed during the growth of Fe on Fe whisker substrates.⁴ The RHEED streak splitting of Fe on Ag(001) sharpened and decreased with increasing substrate temperature and disappeared completely for temperatures greater than 410 K. The amplitude of the RHEED intensity oscillations increased substantially, approximately two to threefold, compared with that observed during the growth at RT. The first period was definitely longer than subsequent periods which were regular and corresponded to 1-ML formation. At a substrate temperature of ~ 420 K, the RHEED streak splitting of Fe disappeared after one additional atomic layer was deposited. The corresponding RHEED patterns were sharp and comparable with those of well-prepared Ag(001) substrates. For our Mössbauer studies, three samples have been prepared:

Ag/5.7Fe/⁵⁷Fe/10Ag/9Au (sample 1) ,

Ag/(5.7Fe/⁵⁷Fe/10Ag)₃/9Au (sample 2) ,

Ag/8.2Fe/⁵⁷Fe/10Ag/9Au (sample 3) .

The last three layers of Fe were grown at 420 K for sample 3 in order to increase the average terrace size at the Fe/Ag(001) interface.

Mössbauer spectra were collected over periods of

weeks using conversion electron Mössbauer spectroscopy (CEMS). The stability of the Mössbauer parameters over that period was as follows: Δ i.s.=0.001 mm/s, Δ QS=0.003 mm/s, and Δ H_{hf} =1 kOe. The i.s. values in this study are reported with respect to a natural iron absorber.

III. RESULTS AND DISCUSSION

The spectrum for the single-multilayer sample 1, obtained after a measuring time of a few weeks, was compared with that of the three-period sample 2 showing the same signal-to-noise ratio. The two spectra are essentially the same. A one-component least-squares fit with one sextet gives virtually the same values for H_{hf} , i.s., and QS. The main difference between the two spectra is that the lines for the three-multilayer sample are on the average 15% wider. In view of the long measuring time and the complexity of the spectrum, it was decided that the linewidth broadening of sample 2 was acceptable, and this sample was studied for a longer time in order to get an adequately resolved spectrum (Fig. 1).

The asymmetry in the line intensities and the asymmetric shape of the lines 1 and 2 in the spectrum indicate the presence of at least two sites for the iron atoms in the neighborhood of the Fe/Ag interface. This result implies that the ⁵⁷Fe atoms are present not only in contact with Ag at the Fe/Ag interface as intended, but also one layer down from the interface. The results of a least-squares fit using two sextets are presented in Table I.

The two sextets have significant different values of H_{hf} , i.s., and QS. The different values of i.s. can be used to identify the two components in the spectrum. Charge-density calculations show that the s -charge density at the ⁵⁷Fe nucleus is expected to be smaller at the Fe/Ag interface than at locations one or more layers below the Fe/Ag boundary.¹ Furthermore, the charge density is already approximately bulklike for iron atoms one layer down. Consequently, we expect for iron atoms at the interface a significantly larger value of i.s. than for atoms one layer down. Comparing this prediction with our CEMS results (Table I), we conclude that sextet 2 is associated with iron atoms at the interface and sextet 1 with atoms one layer below the interface. The relative areas of the two components in the spectrum indicate that only 75% of the ⁵⁷Fe atoms are actually making contact with the Ag atoms at the interface.

From our interpretation, the value of H_{hf} is smaller at the interface than for layers closer to the center of the iron multilayer. This supports the conclusion by Koon *et al.*⁵ for (5.5 Fe/ x Ag) but is different from that of Gutierrez *et al.*⁶ obtained for (6Fe/40Ag). Both these previ-

TABLE I. Values of the isomer shifts (i.s.), the quadrupole splittings (QS) ($eQV_{zz}/4$), the magnetic hyperfine fields H_{hf} , and the relative areas obtained from a two-component fit for Ag(5.7Fe/⁵⁷Fe/10Ag)₃/9Au.

Component	Relative area	H_{hf} (kOe)	i.s. (mm/s)	QS (mm/s)
1	0.25	286	0.06	-0.01
2	0.75	267	0.21	-0.09

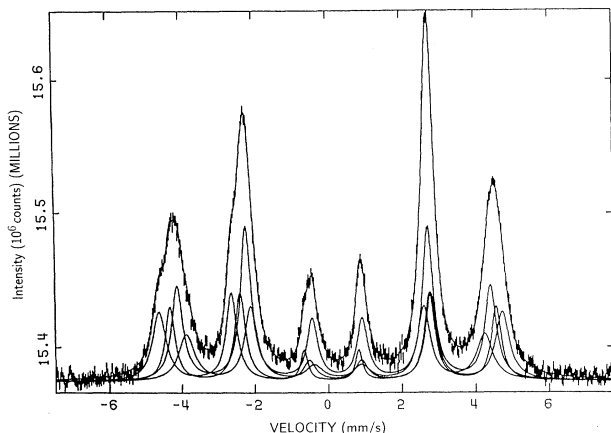


FIG. 1. CEMS spectrum for $\text{Ag}/(5.7\text{Fe}/^{57}\text{Fe}/10\text{Ag})_3/9\text{Au}$ at room temperature. The solid line represents the result of a four-component least-squares fit.

ous results were obtained for multiperiod superlattices where the MES parameters were sampled throughout the width of the iron multilayer. Consequently, these previous spectra show only broadened lines, whereas in the present one at least two components are resolved.

Quantitatively, the i.s. values of our spectrum are in good agreement with those found in vapor-deposited disordered $\text{Fe}_x\text{Ag}_{1-x}$ alloys.^{7,8} Systematic studies have shown that the i.s. in binary Fe-X alloys can be directly correlated to the surface-weighted concentration of the X-atom neighbors of a central iron atom.⁹ For Fe atoms at the interface with four Ag and four Fe nearest neighbors, the Ag surface concentration is about the same as for the $\text{Fe}_{0.5}\text{Ag}_{0.5}$ composition. The average value i.s. ≈ 0.2 mm/s (Refs. 7 and 8) found for this composition agrees well with the value i.s. = 0.21 mm/s found for sextet 2 in the two-component fit.

A close inspection of the two-component fit ($\chi^2=2.2$) shows that the fit is not ideal. Moreover, the linewidths obtained for the two sextets are twice the value found for the iron calibration spectrum. This suggests that more than two sites may be present close to the Fe/Ag interface.

The existence of ^{57}Fe in layers at least one layer down from the Fe/Ag interface already suggests that atoms are deposited on a terraced surface. Considering only the nearest (NN) and next-nearest (NNN) neighbors of a central iron atoms close to the Fe/Ag boundary, the presence of one step terraces leads to the existence of different iron sites at the interface. Position-I Fe atoms refer to sites in the central region at least one atom away from the edge of a terrace (Fig. 2). Position-II Fe atoms are one layer down from the Fe/Ag interface. Site I_t and I_b refer to atoms at the edge of the Fe terraces, i.e., at the top and at the bottom, respectively. Sites I_u and I_d are at the up and down positions at the corners of the terraces where the two atomic steps meet. In this model the concentration of sites I_t and I_b should be equal. The same is true for sites I_u and I_d .

First we attempted a three-component fit. The three

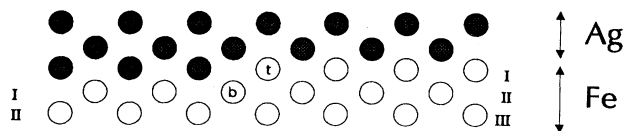


FIG. 2. Five different iron positions I, I_t , I_b , II, and III close to a terraced Fe/Ag(100) interface.

components would correspond to the situation where all iron is present in sites I, I_t , and I_b . This is not very likely because the two-component fit already indicated that the ^{57}Fe atoms are also deposited in sites II on a terraced surface. Nevertheless, a good fit was obtained with three components if the areas of two sextets are constrained to be equal. These two sextets should be associated with Fe sites I_t and I_b . However, after removing the constraints, the least-squares fit with three components produced unacceptable values for the intensity ratios for one of the components.

Next, the spectrum was fitted with four sextets. The four components correspond to iron atoms at sites I, II, I_t , and I_b . Initially, the areas of two sextets corresponding to sites I_t and I_b were constrained to be equal. When a good fit was obtained ($\chi^2=1.26$), the constraints were lifted. The completely free least-squares fit gave the same χ^2 as before and the values of the MES parameters (Table II) did not change significantly. Figure 1 shows the fitted spectrum.

Referring to the discussion of the isomer shift above, we would expect the i.s. values to be different for sites I, I_t , I_b , and II. Fe site I_b has five NN Fe and three NN Ag atoms, site I has four NN Fe and four NN Ag atoms, and site I_t has three NN Fe and six NN Ag atoms. Fe site II has no NN Ag atoms. Since the isomer shift is expected to decrease with a decrease in the surface concentration of the Ag atoms,⁹ we conclude that sextets 1, 2, 3, and 4 can be associated with Fe sites I, II, I_b , and I_t , respectively.

The values of QS in Table II show that an electric-field gradient is present at sites I, I_t , and I_b and possibly a smaller one also at site II. This is expected because the larger size of the Ag atoms will probably destroy the cubic symmetry for the iron atoms close to the Fe/Ag boundary. For instance, for site I, one would expect a tetragonal distortion. Maintaining a fourfold symmetry in the plane of the interface would cause $V_{xx}=V_{yy}=0$ and V_{zz} to be perpendicular to the interface. Information about the direction of magnetic moments can be obtained from the relative intensities of the Mössbauer lines, which is given by $3:x:1$, where

$$x = 4 \sin^2 \theta / (1 + \cos^2 \theta),$$

and θ is the angle between the incident γ -ray direction and the direction of the magnetic moment of the iron atom. From the total area ratio, we calculate $x=3.84$, which is consistent with the magnetization direction moments lying in the plane of the interface ($\theta=90^\circ$) when

TABLE II. Values of the isomer shifts (i.s.), the quadrupole splittings (QS), the magnetic hyperfine fields H_{hf} , and the relative areas obtained from a four-component fit for $\text{Ag}/(5.7\text{Fe}/^{57}\text{Fe}/10\text{Ag})_3/9\text{Au}$.

Component	Relative area	H_{hf} (kOe)	i.s. (mm/s)	QS (mm/s)
1	0.38	267	0.21	-0.10
2	0.19	292	0.06	-0.02
3	0.21	278	0.15	-0.06
4	0.21	253	0.23	-0.06

the solid angle of the γ beam is taken into account. This leads to

$$|eQV_{zz}/4| = 0.09 \text{ mm/s}$$

for site I. For the Fe atoms at sites I_t and I_b at the edge of the terraces, the symmetry is further reduced. For site II we expect a much smaller tetragonal distortion because Fe atoms one or more layers away from the interface should rapidly regain the cubic symmetry of the bulk iron. This is consistent with the small value of QS found for component 2 in the spectrum. The results are in fairly good agreement with those presented earlier for a multiperiod structure probed with a 2-ML ^{57}Fe layer.^{10,11}

Table II indicates that a fraction 0.19 of ^{57}Fe atoms is located one layer down from the Fe/Ag boundary; a fraction 0.81 makes contact with the Ag atoms. Of these, a fraction 0.26 is located at the edge of a terrace, i.e., at positions I_t or I_b . This information can be used to find the average terrace size. A $n \times n$ terrace would have a fraction of $(4/n - 4/n^2) = 0.26$ iron atoms located at the edge of the terrace. From this we calculate $n = 14.3$ with an average terrace edge of 4 nm. This conclusion is consistent with the observations of the RHEED streak splittings that were discussed in Sec. II. For the size of these terraces the concentration of positions I_u and I_d can be neglected in the analysis of the CEMS spectrum.

By increasing the terrace size at the interface, the relative areas of components I_t and I_b should decrease if the model described above is correct. This can be accomplished by depositing the atomic layers at a higher temperature. Figure 3 shows the CEMS spectrum obtained for

Ag/8.2Fe/ ^{57}Fe /10Ag/9Au

(sample 3), where the last three atomic layers of iron were grown at 420 K. The results of a three-component fit are shown in Fig. 3 and Table III. A study of the i.s. and QS values indicates that component 1 represents Fe atoms at the interface. Components 2 and 3, on the other hand, correspond to iron atoms that do not make contact with the Ag atoms. Probably, they represent iron atoms in the second and third layers, respectively, below the Fe/Ag interface. Apparently, the terraces are so extensive that no indications of the presence of iron atoms located at the edges of terraces can be seen in the CEMS spectrum. Because components 3 and 4 in the spectrum of Fig. 1 are no longer present, the interface component 1 in Fig. 2 can now clearly be resolved from components one or more layers below the interface. This confirms the validity of the model proposed for the spectrum obtained for

sample 2 (Fig. 1).

The combined relative areas of components 2 and 3 corresponding to ^{57}Fe sites at layers II and III below the Fe/Ag interface is 42% for sample 3. This value is much larger than the value of 19% found for ^{57}Fe at layer II in the sample 2 grown at room temperature. This result demonstrates the importance of diffusion of the ^{57}Fe into the underlying Fe layers while the ^{57}Fe is being deposited at the surface at a temperature of 420 K.

From spin-density calculations¹ we expect that the magnetic hyperfine fields at 0 K vary across the width of the iron multilayer. This has been observed by Tang *et al.*¹⁰ and Keavney *et al.*^{11,12} although the results of these investigations are not consistent with each other. Also, MES investigations of disordered $\text{Fe}_x\text{Ag}_{1-x}$ alloys show that H_{hf} depends on the local distribution of Ag atoms around a central Fe atom.^{7,8} The value of H_{hf} at 300 K, furthermore, is determined by the strength of the local exchange interaction. This generally depends in iron alloys on the number and type of nearest neighbors.¹³ As a result, the various components corresponding to different Fe sites may be best resolved at a particular value of T/T_c .

Interestingly, the magnetic-hyperfine-field distribution has shifted to higher values for the sample prepared at 420 K. Apparently, the Curie temperature T_c of this sample is higher than that of the sample grown at 300 K. The increase may be explained in the first place by the thicker iron multilayer (9.2 ML versus 6.7 ML) and secondly by the larger terraces in the heated sample.

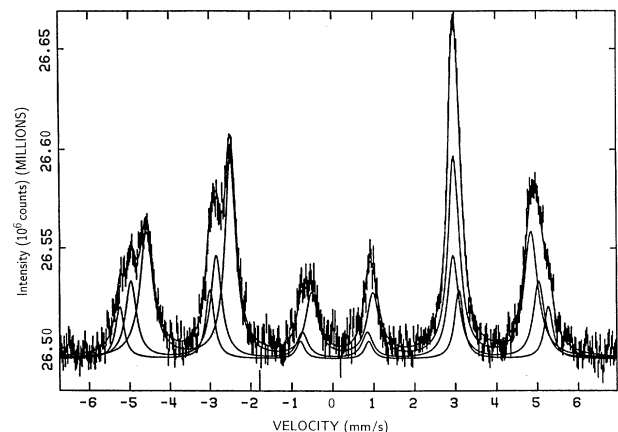


FIG. 3. CEMS spectrum for $\text{Ag}/7.7\text{Fe}/^{57}\text{Fe}/10\text{Ag}/9\text{Au}$. The solid line represents the result of a three-component least-squares fit.

TABLE III. Values of the isomer shifts (i.s.), the quadrupole splittings (QS), the hyperfine magnetic fields H_{hf} , and the relative areas obtained from a three-component fit for Ag/8.2Fe/1⁵⁷Fe/10Ag/9Au.

Component	Relative area	H_{hf} (kOe)	i.s. (mm/s)	QS (mm/s)
1	0.58	293	0.20	-0.10
2	0.28	311	0.05	-0.02
3	0.14	327	0.03	-0.03

Both have the effect of strengthening the effective exchange interaction in the iron multilayer.

This result indicates that a comparison of the H_{hf} values in Tables III and IV with values found in the literature may only be valid if the samples have the same structure and are grown at the same temperature. It is not surprising, therefore, that the H_{hf} distribution for the present sample differs from that found by Tang *et al.*¹⁰ and Keavney *et al.*^{11,12} for [9Fe(100)/40Ag] multiperiod structures. Furthermore, these structures were investigated by using a 2-ML ⁵⁷Fe probe layer. This explains the larger linewidths found in the spectra obtained for these samples compared to our spectra. The 2-ML ⁵⁷Fe probe layer samples the MES parameters over more atomic layers in the Fe multilayer than a 1-ML ⁵⁷Fe probe layer. In other words, a 2-ML ⁵⁷Fe probe layer provides significantly less resolution than a 1-ML ⁵⁷Fe probe layer.

The necessity of using a 1-ML ⁵⁷Fe as probe layer is also emphasized by Liu and Gradmann¹⁴ in a recent study of the Fe(100)/Ag(100) interface in W/40Fe/Ag structures. The values of H_{hf} at 300 K for these structures are much higher than those found for sample 2 and slightly higher than observed for sample 3. This is consistent with the difference in Fe multilayer thickness and the heat treatment of the two sets of samples. Two components were recognized in the Mössbauer spectra obtained for W/40Fe/Ag. This may be explained from the fact that the ⁵⁷Fe probe layer was deposited at an Fe multilayer previously grown at 500 K.¹⁴ At this temperature the terraces on which the ⁵⁷Fe is deposited are relatively large. Consequently, the components associated with Fe sites I_t and I_b may be too small to be recognizable, similar to the results obtained for sample 3. The ⁵⁷Fe was subsequently deposited at 90 K. At this temperature the

growth occurs by the formation of atomic island clusters, explaining the presence of almost 60% of ⁵⁷Fe in Fe sites II and the remainder in Fe site I.

IV. SUMMARY

A Mössbauer-effect-spectroscopy study of the Fe(001)/Ag(001) interface in molecular-beam-epitaxy-grown structures has been performed by using a monolayer of ⁵⁷Fe as a probe layer. This method provides adequate resolution in the Mössbauer spectrum for recognizing the existence of terraces at the Fe/Ag interface. The size of the terraces is increased by depositing the upper Fe monolayers at 420 K. Three Fe sites are found to be present at the Fe/Ag interface. These Fe sites are distinguished from each other by different values of H_{hf} . From the intensity of the three components in the Mössbauer spectrum, the average size of the terraces was estimated. The i.s. and QS values for Fe sites at the Fe/Ag interface are significantly different from those obtained for Fe sites one or more layers removed from the interface. A diffusion of the ⁵⁷Fe atoms into lower Fe layers is observed when the ⁵⁷Fe atoms are deposited at 420 K. The magnetic-hyperfine-field distribution depends on the number of nearest Fe and Ag neighbors and also on the thickness of the Fe multilayers and the roughness of the Fe-Ag interface.

ACKNOWLEDGMENTS

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