

GdFe₂ alloy formation studied on the atomic scale by scanning tunneling microscopy

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Well-ordered GdFe₂ alloy films of up to two ML thickness were grown on top of a W(110) substrate and characterized by using scanning tunneling microscopy/spectroscopy (STM/STS) and low-energy electron diffraction (LEED). The crystallographic structure of the ultrathin films was found to be different from the well-known bulk structure (C15 Laves phase). This is supposed to result from the influence of the substrate on the growth behavior. Based on atomically resolved STM images and LEED studies, a structure model for the ultrathin GdFe₂ films on W(110) is proposed. [S0163-1829(99)04347-7]

I. INTRODUCTION

Alloys of 3*d* transition metals with 4*f* rare earth metals, as, e.g., FeGd and FeTb, are of intense technological interest because they exhibit outstanding magnetic properties. The Curie temperature of alloys of Gd or Tb with Fe as well as their coercivity can be tuned over a wide range by changing the mixing ratio.¹ This behavior, in combination with a strong magneto-optical effect, makes them of particular interest for magneto-optical storage. Furthermore crystalline alloys, especially TbFe₂, exhibit a strong magnetocrystalline anisotropy resulting in an easy magnetization direction being perpendicular to the film plane in thin film systems.² A perpendicular anisotropy is also present in the amorphous alloys.³ Films with perpendicular magnetization direction allow on the one hand enhanced writing densities as well as on the other hand an increased signal-to-noise ratio. Another aspect of technological interest are magnetostrictive properties of 3*d*/4*f* alloys like TbFe₂, DyFe₂, and Dy_{0.7}Tb_{0.3}Fe₂ (Terfenol-D). For such applications, the preparation of single-crystalline thin films is of importance because a well defined orientation of the crystallographic directions is needed to make use of the magnetostrictive effect in small devices.

While the magnetic and magnetostrictive properties of the bulk material in dependence of the fabrication process, especially for Terfenol-D, are well understood, very little is known about thin film properties. Until now, only some attempts have been made to grow very thin crystalline films of 3*d*/4*f* alloys. TbFe₂ (Ref. 4) and YCo₂ (Ref. 5) have been grown on sapphire with Mo(110) and W(110) buffer layers, respectively. In both cases twin formation occurred. Oderno *et al.* recently succeeded in preparing DyFe₂, TbFe₂, and Dy_{0.7}Tb_{0.3}Fe₂ epitaxial thin films on sapphire with a Nb(110) buffer layer.⁶ M. Huth *et al.* presented results on the preparation of well-ordered epitaxial films of TbFe₂ on sapphire substrates with a Mo(110) buffer layer.⁷ On the other hand, most of the experiments on the magnetic thin film properties of the pure elements Fe, Gd, and Tb have been carried out for films grown on W(110). The growth of these films from the submonolayer coverage⁸⁻¹⁰ range to thick films is well understood and forms the basis for understanding the mag-

netic properties. The experiments presented in this paper turn the attention to the following questions: What does the initial state of 3*d*/4*f*-alloy formation on W(110) look like? Is it possible to grow epitaxial films of GdFe₂ on W(110) without additional buffer layers? What is the influence of the substrate on the growth behavior and what consequences on the crystallographic structure will result from this? Which crystallographic orientation will the film grow in?

In the following, we present a study on the epitaxial growth of very thin films of GdFe₂ on a W(110) single crystal carried out by low-energy electron diffraction (LEED) and scanning tunneling microscopy/spectroscopy (STM/STS). We will show that the epitaxial growth of up to two monolayer (ML) thick films of GdFe₂ is possible on W(110). The crystallographic structure of the films with a thickness of up to two monolayers was found to be different from the GdFe₂ bulk structure (Laves phase C15). Based on our atomically resolved STM images and LEED data we propose a structure model for the ultrathin GdFe₂/W(110) films.

II. EXPERIMENTAL DETAILS

The experiments were carried out in a two-chamber UHV system with a base pressure below 1×10^{-10} torr. The rare earth metal Gd was evaporated from a W crucible heated by electron bombardment. Fe was evaporated from a commercial *e*-beam evaporation source. The evaporators were repeatedly calibrated with submonolayer accuracy via STM by growing pure films of Gd or Fe. Consequently, we could ascertain the amount of evaporated metal by about ± 0.2 ML for the very thin films of GdFe₂. The exact amount was determined afterwards via STM. The W(110) single-crystal substrate was prepared as described earlier.¹¹ During thin film evaporation the pressure did not exceed 5×10^{-10} torr. After preparation the samples were transferred into a separate analysis chamber with a base pressure below 1×10^{-11} torr. All topographic STM images were measured in the constant-current mode. The scanner was calibrated on the well known Gd/W(110) superstructures.¹²⁻¹⁴ The ionic radii of Gd and Fe differ significantly from each other. The first ML of Fe on W(110) that grows pseudomorphically holds 1.56 times the number of adsorbate atoms compared with the first ML Gd/W(110). For this reason, the amount of

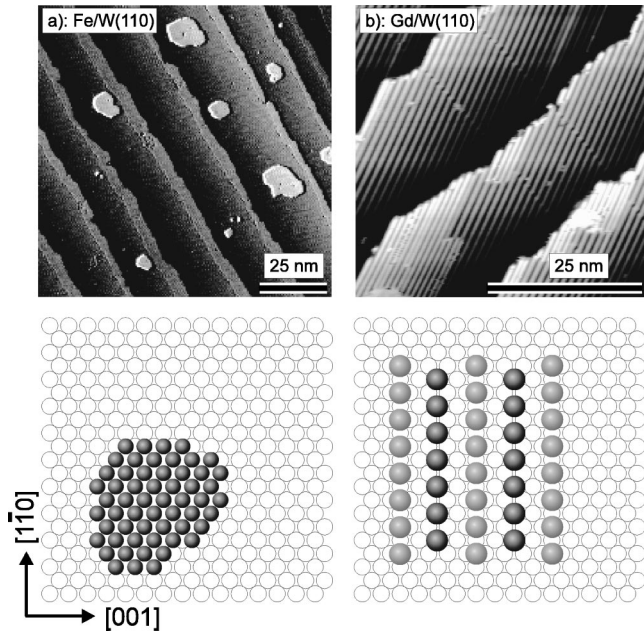


FIG. 1. Comparison of the growth of Fe (a) and Gd (b) on W(110) in the submonolayer coverage regime. For both metals the coverage is about 0.25 ML. The scan range for both images is 70 nm \times 70 nm. Below the STM images structure models are shown to highlight the difference in the growth mode.

evaporated material is given in substrate units to preserve the mixing ratio to be directly comparable. The first closed monolayer of Gd on W(110) holds 0.64 monolayers as measured in substrate units; the first closed monolayer of Fe on W(110) that grows pseudomorphically consequently holds 1 monolayer in substrate units.

III. RESULTS AND DISCUSSION

Both elements, Fe and Gd, exhibit Frank–van der Merwe or Stranski-Krastanov growth depending on the film thickness and annealing temperature in the coverage range above one monolayer.^{8–10} The thin film growth behavior of the two metals in the coverage regime below one monolayer differs drastically from each other. This is demonstrated in Fig. 1 where two samples of both metals in pure form, prepared under similar conditions, are presented. While Fe [Fig. 1(a)] exhibits the formation of one monolayer film patches as well as stripes of material growing along the substrate steps (step flow growth),^{8,9} the Gd atoms [Fig. 1(b)] tend to cover the W(110) surface as quasi-one-dimensional superstructures.^{12,13}

The reason for this behavior of the Gd atoms is a strong difference in electron affinity between the W(110) substrate and the electropositive Gd atoms triggering a charge transfer from the Gd atoms to the substrate. The resulting dipole moment of the individual atoms induces a repulsive dipole-dipole interaction within the layer giving rise to the formation of evenly spaced chainlike superstructures. The distance between the chains decreases in discrete steps with increasing coverage. These chainlike superstructures coincide with the appearance of ($n\times 2$) LEED patterns ($n=10,8,7,6,5$). The sample presented in Fig. 1(b) mainly shows the (8

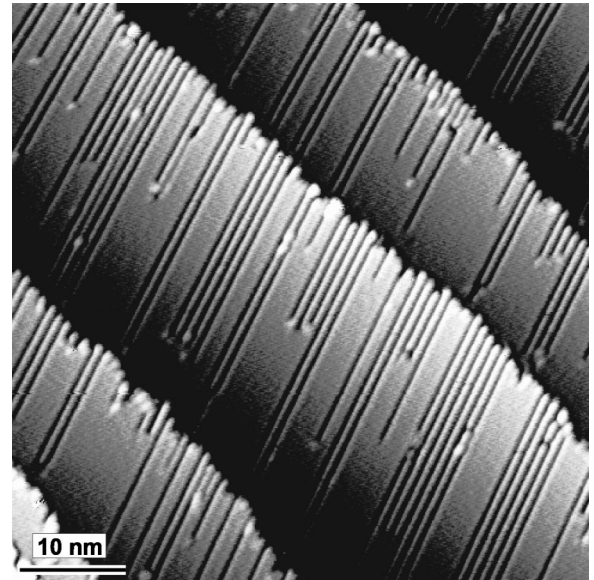


FIG. 2. Constant current STM image of an alloy of approximately 0.3 ML Gd and 0.4 ML Fe. The striped areas represent the well-known Gd superstructures with the stripes being aligned along the [001] direction of the substrate. The smooth areas correspond to an alloy of GdFe₂. The scan range is 70 nm \times 70 nm. Sample bias: $U=0.2$ V, tunneling current $I=0.3$ nA.

$\times 2$) superstructure. If the periodicity exceeds 15 Å, a stable imaging of the Gd chains is not possible. This is in agreement with previous results obtained via low energy electron diffraction showing that no stable superstructures with periodicities larger than for the (10 \times 2) could be observed.¹³ At a coverage corresponding to $\Theta\approx 0.35$ monolayers a closed, pseudohexagonal $c(5\times 3)$ structure is formed. Additional coverage results in the first closed monolayer of Gd on W(110). It represents a coverage of $\Theta\approx 0.64$ monolayers; its nearly hexagonal symmetry reflects the symmetry of the Gd(0001) lattice.

Given these two elements, Gd and Fe, differing drastically from each other in their thin film growth behavior on W(110), the question arises which growth mode an alloy of the two components will show and which stoichiometry is the most stable one on top of the W(110) surface. Figure 2 shows a topographic STM image of an alloy of 0.3 ML Gd and 0.4 ML Fe. The sample was prepared by evaporating 0.3 ML Gd onto the substrate held at 400 K and subsequently by an additional evaporation of 0.4 ML Fe. Post annealing was performed at 700 K for 5 min. The substrate is covered by a film consisting of two different kind of domains, a striped one with the stripes running along the $[1\bar{1}0]$ direction of the substrate being typical for Gd, as well as a smooth one. This sample exhibited a LEED pattern labeled as $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ not known from pure Gd or Fe films. In view of the mixing ratio and the assumption that the striped areas consist mainly of Gd, the smooth areas are expected to consist of an alloy with a mixing ratio of Gd to Fe to be 1:2. To strengthen this hypothesis, a sample was prepared that holds 0.3 ML of Gd and 0.6 ML of Fe. The preparation steps as well as the annealing procedure was the same as for the sample displayed in Fig. 2.

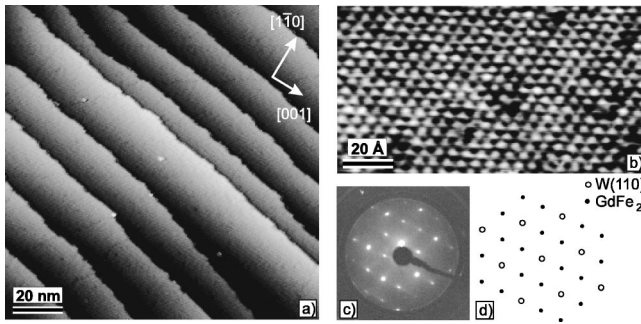


FIG. 3. (a): Completely closed and smooth first ML of GdFe₂ on W(110). (b): Atomic resolution obtained on this sample at a sample bias of $U=0.18$ V and a tunneling current of $I=3$ nA. (c): Photograph and (d): sketch of the $(\frac{2}{1} \frac{1}{2})$ LEED pattern of this sample. The crystallographic directions are the same for all figures.

Figure 3(a) shows the resulting sample topography. The substrate is completely covered by a smooth film with the underlying W(110) substrate steps visible. The LEED pattern of this sample corresponds to a sharp $(\frac{2}{1} \frac{1}{2})$ superstructure. A photograph of the LEED pattern as well as its interpretation is presented in the Figs. 3(c) and 3(d), respectively. The atomic distances as determined from the diffraction pattern is 9.48 \AA in the $[001]$ direction and 4.47 \AA in the $[1\bar{1}0]$ direction of the substrate. The same periodicity as in the LEED pattern can be found in atomically resolved STM images of the first ML GdFe₂. Figure 3(b) shows a part of the sample presented in Fig. 3(a) atomically resolved at 180 mV sample bias and 3 nA tunneling current. Based on the LEED and STM data as well as on the stoichiometry of the prepared films we present a structure model for the alloy, as shown in Fig. 4. All atoms are drawn to scale of their metallic radii. In our model we have placed the Gd as well as the Fe atoms on bridge sites with respect to the underlying W(110). We assume this to be the energetically favorable adsorption site for both atomic species, since recent work could show this to be true for Fe on W(110).¹⁵ Comparing the structure model with

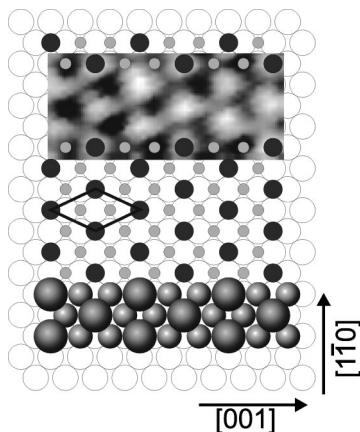


FIG. 4. Structure model for the first ML GdFe₂ on W(110). Gd is represented as large, Fe as small balls. The atoms are scaled down by a factor of two for better clarity of the registry between substrate and adsorbate. In the lower part of the model the atoms are drawn to scale. A part of an atomically resolved STM image is inserted in the structure model at the same scale.

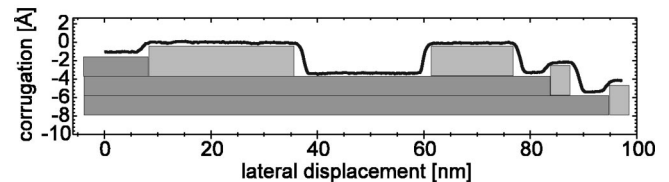
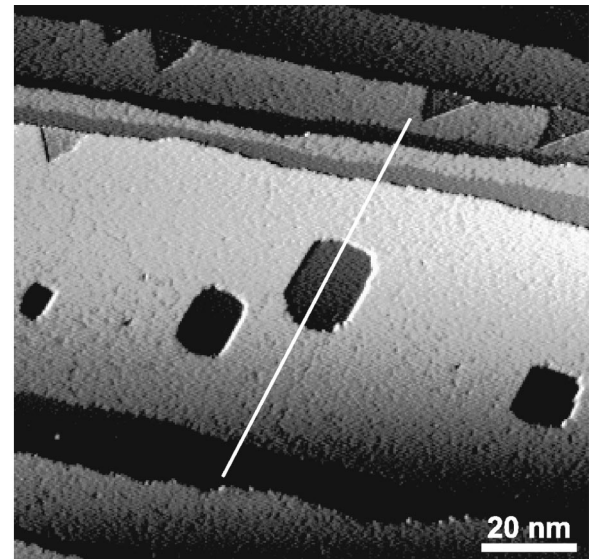


FIG. 5. Approximately 0.75 ML GdFe₂ growing in step flow along the W(110) step edges. Rectangular holes in the film are oriented along the $[001]$ and $[1\bar{1}0]$ directions of the substrate. From the line section indicated in the image the monoatomic step height is determined to be 3 \AA from the top of the bare tungsten substrate to the top of the first ML GdFe₂. The scan range is $135 \text{ nm} \times 135 \text{ nm}$, the tunneling parameters are $U=-0.24$ V, $I=0.2$ nA.

the atomic scale STM images, it becomes clear that we do only see one atomic species of the alloy, the Gd atoms. The fact, that the Gd atoms are much larger than the Fe atoms may play a major role, but a definite statement concerning this point can only be given if local density of states (LDOS) calculations for this structure will become available.

The preparation of samples consisting of less than one ML GdFe₂ results in a W(110) substrate partially covered by the first ML GdFe₂, as can be seen in Fig. 5. The substrate was held at room temperature during evaporation of 0.25 ML Gd. After the additional evaporation of 0.5 ML Fe, the sample was post-annealed at 700 K for 5 min. The one ML thick GdFe₂ film grows along the substrate steps (step flow growth). However, some rectangular holes in the film being oriented along the main crystallographic directions of the substrate remain. The line section indicates the monoatomic step height from the substrate to the top of the first ML of the alloy to be 3.0 \AA as seen by STM in the constant current mode of operation.

The growth of the GdFe₂ structure could be continued to the second ML by evaporating approximately 0.5 ML of Gd and 1 ML Fe and subsequent annealing to 500 K. The resulting sample topography is shown in Fig. 6. Again, the substrate is completely covered by a smooth alloy of Gd and Fe but additionally patches of the second ML GdFe₂ are

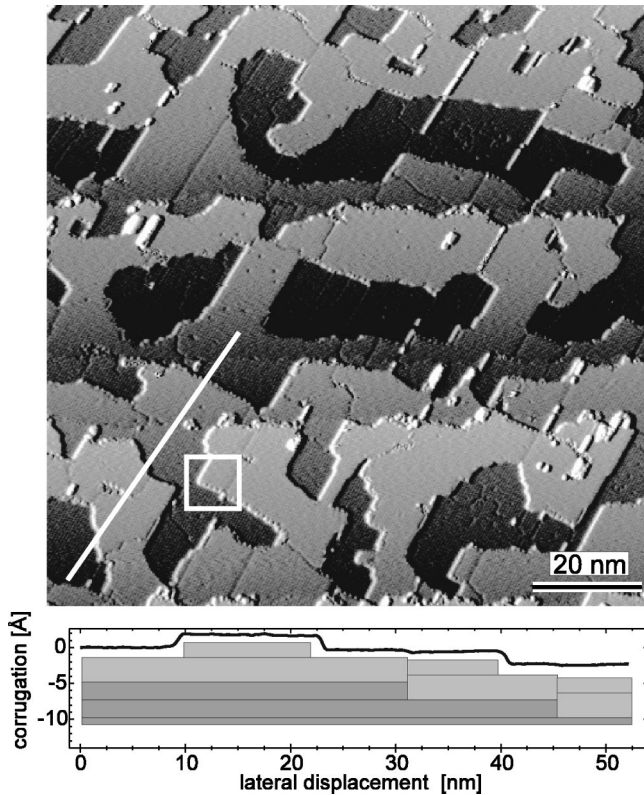


FIG. 6. First and second ML GdFe_2 on $\text{W}(110)$. In the area marked with a box we obtained atomic resolution. From the line section the monoatomic step height between the first and second layer of GdFe_2 can be determined to be only 1.9 \AA .

present. A line section taken from this image is shown together with a sketch of the cross section of the sample.

Figure 7 displays the tunneling spectroscopy measurements that were carried out on this sample. The given differential conductivity dI/dU is a direct measure of the local density of states (LDOS). Within the error of the measurement there is no difference between the first and the second ML GdFe_2 . This observation reflects the identical geometric arrangement of the alloy in both layers (see below).

In the area marked by a frame in Fig. 6 we could achieve atomic resolution on top of the first as well as on the second monolayer simultaneously. These data are presented in Fig. 8(a). The atomic structure of the first and the second ML looks similar. This is consistent with the observation of similar tunneling spectra. Using the atomically resolved images we are able to investigate the positions of the atoms of the second ML with respect to the atoms of the first ML by using a registration grid. Again we assume the maxima visible in

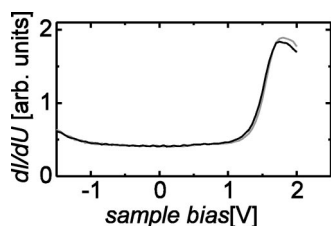


FIG. 7. Differential conductivity dI/dU obtained on the first (grey) and second (black) ML GdFe_2 on $\text{W}(110)$. The stabilization parameters are $U=2 \text{ V}$, $I=0.5 \text{ nA}$.

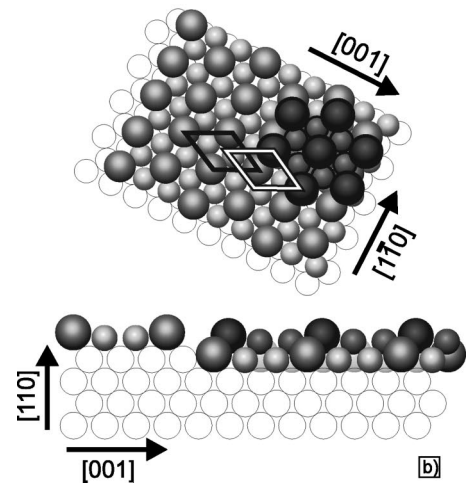
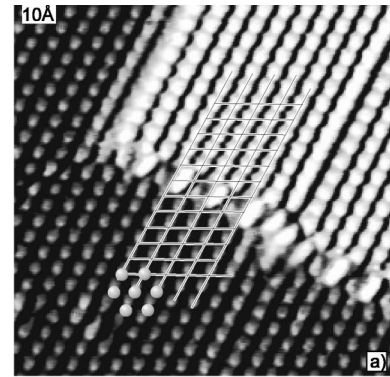


FIG. 8. (a) Atomic resolution on the first and second ML GdFe_2 on $\text{W}(110)$ obtained at $U=55 \text{ mV}$ and $I=3 \text{ nA}$. The grating and the balls are the result of a procedure to determine the registry between the atoms of the first and the second ML. (b) Structure model in top and in side view of the first and second ML GdFe_2 on $\text{W}(110)$ deduced from the atomically resolved STM images.

the atomically resolved STM images to represent the Gd atoms. The resulting structure model [Fig. 8(b)] shows the Gd atoms of the second ML residing on top of the first ML Fe atoms. This atomic arrangement is also assumed to be the reason for the extraordinary small monoatomic step height of 1.9 \AA between the first to the second ML GdFe_2 (see Fig. 6), being lower than the monoatomic step height of the $\text{W}(110)$ substrate (2.24 \AA).

In the next step our structure model for ultrathin GdFe_2 films is compared with the known crystallographic structure of bulk GdFe_2 , the so-called C15 Laves phase being a complicated arrangement of the two atomic species (for further details see, e.g., Ref. 16). We could find no crystallographic direction with low indices of the Laves phase corresponding to the model we deduced as a result of our STM and LEED data. This is not surprising, because the first as well as the second ML grows pseudomorphically, i.e., the atomic arrangement in the alloy is mainly determined by the substrate, resulting in a relatively large deviation of the atomic positions when comparing the deposited film and the bulk Laves phase. The geometric arrangement of the Gd atoms in the GdFe_2 films of up to two ML thickness appears to resemble

the (111) plane of the C15 Laves phase, compressed by 14% in the $[1\bar{1}0]$ direction of the W(110) substrate and strained by 5.3% in the $[001]$ direction. However, the arrangement of the Fe atoms with respect of the Gd atoms is completely different from the bulk structure. Assuming a release of this deviation with growing film thickness it can be expected that the C15 Laves phase develops at larger film thickness of GdFe₂ on W(110) as deduced for TbFe₂ on Mo(110).⁷ This would imply the existence of a structural phase transition in the GdFe₂ system being the subject of current investigations.

IV. SUMMARY

In summary, we have presented an atomic scale study of the very early stages of GdFe₂ alloy formation on W(110).

The first ML GdFe₂ grows in a step flow growth mode on top of the W(110) substrate. We were able to prepare and atomically resolve the second ML as well. A structure model based on LEED and atomically resolved STM data was developed for the first and second ML of GdFe₂. Tunneling spectroscopy measurements showed no difference between the first and the second ML of GdFe₂. The atomic structure of the ultrathin films was found to be different from the bulk structure of the GdFe₂ (C15 Laves phase).

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