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Scanning tunneling microscopy and spectroscopy on thin Fe₃O₄ (110) films on MgO

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Thin Fe₃O₄ (110) films, grown by molecular-beam epitaxy on MgO, have been studied by scanning tunneling microscopy and spectroscopy. A 500-Å-thick film was cleaned prior to the measurements by annealing at 850 K under ultrahigh vacuum. Tunneling images show the onset of the formation of the one-dimensional row reconstruction, which was previously also observed on surfaces of bulk single crystals cleaned by ion bombardment and subsequent annealing. Spectroscopic current-voltage curves reveal different behavior depending on the location of the tip above the row reconstruction. Most notably, when probing the filled states at negative sample bias, a larger current was found on top of the rows as compared to a tip position between two rows. © 1996 American Vacuum Society.

I. INTRODUCTION

In the last decade a considerable effort has been directed toward the growth of artificial layered structures. The continuous improvement of deposition techniques has allowed one to prepare not only metallic (magnetic) multilayer structures, but recently also thin oxide films and multilayers.¹⁻⁵ As compared to pure metals and their alloys, the main interest in oxides stems from the rich variety of magnetic properties and electronic configurations they exhibit, in addition to their chemical stability. Oxide ferrites are particularly interesting because of applications such as microwave devices and recording media. By growing these in the form of thin films or multilayers, their properties might be manipulated, offering an alternative to the usually employed chemical substitutions.

As a magnetic spinel, magnetite (Fe₃O₄) has received a lot of attention. For example, Fe₃O₄ thin films have been prepared on MgO single crystal substrates by molecular-beam epitaxy (MBE). These layers were shown to grow coherently in the correct phase,⁵ i.e., without unwanted phases such as Fe, FeO, and Fe₂O₃. For these films it was also found⁶ that the magnetic properties compare well with those of bulk Fe₃O₄, although the Verwey transition was found at a somewhat lowered temperature with respect to the bulk value^{7,8} of 124 K. In addition to the growth of thin films, oxide superlattices have been grown as well. In this case the magnetic Fe₃O₄ layers are separated by insulating and lattice matching oxide layers, such as NiO,^{3,4} CoO,^{5,9} or MgO.¹⁰

In this contribution we report on scanning tunneling microscopy and spectroscopy results obtained on the (110) surface of a 500-Å-thick Fe₃O₄ film grown on MgO. As previously outlined,^{11,12} on this particular surface Fe ions from both of the two antiferromagnetically coupled spin sublattices are present. Together with the high spin polarization at the Fermi level¹³⁻¹⁵ and the good room-temperature conductivity, this provides an ideal test surface for spin-sensitive

scanning tunneling microscopy (STM); however, in our previous attempt to prepare a clean and well-ordered (110) surface using bulk single crystals, the surface was found to reconstruct in the form of rows of double-layer height.¹² This complication might have resulted from the preparation procedure used, consisting of ion bombardment and subsequent annealing at temperatures as high as 1200 K. For the MBE-grown film used in this study, only annealing at lower temperatures was applied, in an attempt to prepare a bulk terminated surface. The results of structural investigations with STM are presented in the following.

II. EXPERIMENT

The Fe₃O₄ films were deposited by e-beam evaporation from Fe targets in a MBE system, with the MgO substrate at a temperature of 525 K and an oxygen pressure of 2×10^{-5} mbar. More details about the growth of Fe₃O₄ layers in different orientations can be found in Ref. 5. The films were transported through air to another ultrahigh-vacuum (UHV) system with a base pressure below 5×10^{-11} mbar. In this system, containing a homebuilt STM, the chemical state of the surface was investigated by Auger electron spectroscopy (AES), prior to annealing at about 850 K using electron bombardment from the back side of the sample holder. The sample temperature was estimated from the temperature of the metallic sample holder, which was measured with an infrared pyrometer. This results in an uncertainty of ± 50 K due to the stray radiation from the heating filament transmitted through the sample. After annealing the film was inspected by AES again and transferred to the STM. Images were obtained using Pt-Ir tips in the constant-current mode. Current-voltage (I-V) curves were obtained by sweeping the bias voltage with the current regulation system disabled.

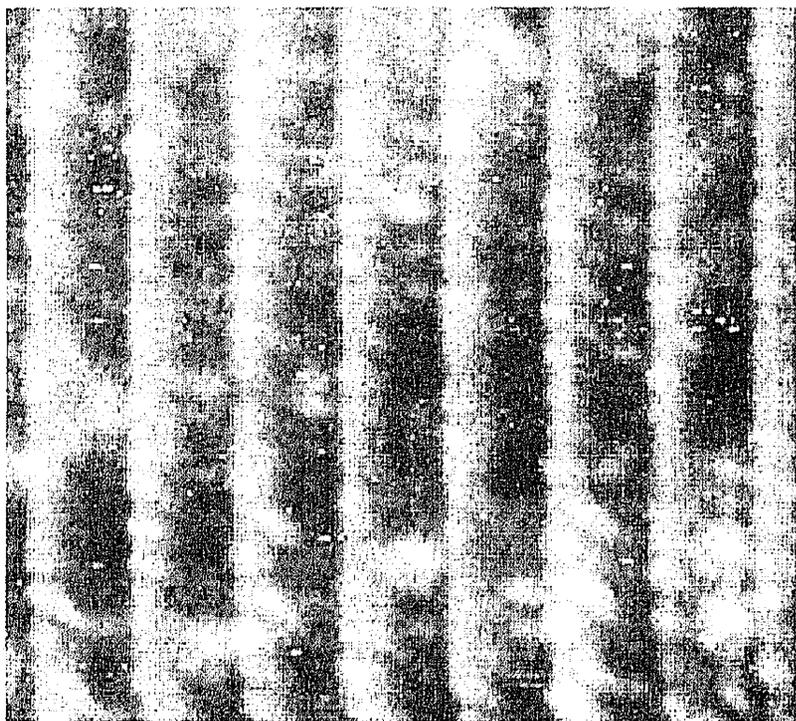


FIG. 1. STM image of the (110) surface of a bulk Fe₃O₄ crystal, prepared by ion bombardment and annealing at 1200 K. Scan size: 200×200 Å²; sample voltage: +2.0 V; tunnel current: 20 pA.

III. RESULTS

After exposure to air, AES revealed carbon contamination of 60% and on the order of 1% of S and Cl. At first, cleaning was tried at conditions similar to those during growth, i.e., at temperatures around 500 K and 1×10^{-5} mbar oxygen partial pressure. As no reduction of the contamination levels was detected, the temperature was gradually increased, where the final step consisted of 10 min at 850 K in the residual oxygen partial pressure below 10^{-12} mbar. Then the contamination levels of C, S, and Cl were reduced to the detection limit of the AES system. However, a significant amount of Mg was detected resulting from diffusion from the substrate; for the Mg/Fe ratio a value of 0.6 was found, which should be treated as an indication rather than an absolute concentration ratio, since we have not calibrated the relative sensitivity of our AES system for different elements. Also the O/Fe ratio of 2.1 was larger than the 1.6 found before annealing.

For comparison, we will briefly recapitulate the STM results obtained on the (110) surface of bulk Fe₃O₄ crystals. For these crystals a clean and regular surface could be prepared by Ar⁺-ion bombardment at 1 keV followed by annealing for 10 min at 1200 K. A typical example of tunneling images obtained on this surface is displayed in Fig. 1, showing rows running in the $(\bar{1}10)$ direction with a separation of 25 Å. The image also shows regular atomic features along the rows, previously identified as octahedrally coordinated Fe atoms.¹² It was argued that this reconstruction might be driven by a favored surface termination in the higher oxidation phase α -Fe₂O₃, which, however, cannot be matched smoothly to the underlying Fe₃O₄ lattice. A structural model was proposed where the rows contain only octahedrally but no tetrahedrally coordinated Fe and a higher O/Fe ratio, as in α -Fe₂O₃.

A STM image obtained on the surface of the MBE-grown thin-film sample is given in Fig. 2. The 1000×1000 Å² image was recorded with a 50 pA tunnel current at +2.0 V

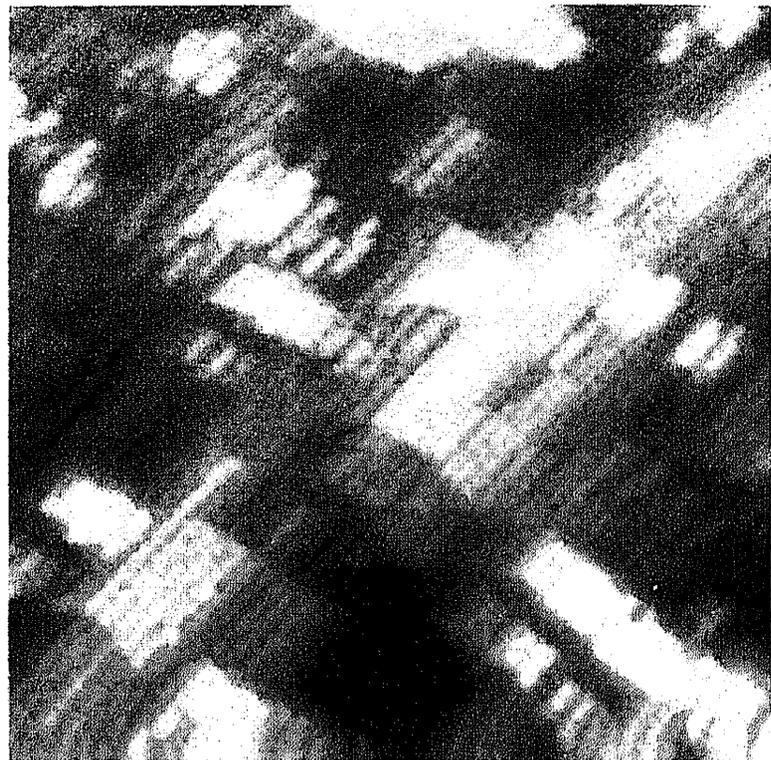


FIG. 2. STM image of a 500-Å-thick (110)-oriented Fe₃O₄ film on MgO, after annealing at 850 K. Scan size: 1000×1000 Å²; sample voltage: +2.0 V; tunnel current: 50 pA.

sample bias. Although the surface is not as regular and flat compared to that of the bulk crystals, the tendency toward the formation of rows with more or less the same orientation is evident. The mutual distance between rows is spread out over values ranging from 20 to 40 Å, and vertical height differences go up to 40 Å. These results are similar to those observed on bulk crystals which were after Ar⁺-ion bombardment annealed to only 850 K, as was done for the thin-film sample.

In one of the small regular parts of the surface, I-V curves were recorded as a function of the local position of the tip above the rows. At every location where a I-V curve was measured, the current was first stabilized at 100 pA. The resulting regulation signal was used to produce a conventional image, which is presented in the inset of Fig. 3. A total of 100 I-V curves was averaged in each of the two regions indicated by line 1 (above a row) and line 2 (between two rows). The resulting averaged curves 1 and 2, respectively, are displayed in Fig. 3. The main features are a region of approximately 2 eV around $V=0$ with almost no current, and an asymmetry of the current with respect to the bias polarity. This is comparable to results on bulk samples reported earlier.^{11,12} The main difference between curves 1 and 2 appears in the region of negative sample bias, with the current being significantly larger for the tip positioned above a row (i.e., for curve 1). The current at -2.0 V is a factor of three larger for the tip positioned above a row. For this bias polarity, electrons are tunneling from the Fe₃O₄ sample to the tip, so that the filled states of the Fe₃O₄ are probed.

IV. DISCUSSION

We have seen that annealing at 850 K without Ar⁺-ion bombardment, as applied to the MBE-grown thin-film sample, produces a similar surface structure as observed on bulk crystals prepared by annealing at 850 K after Ar⁺-ion bombardment cleaning. This shows that the ion bombard-

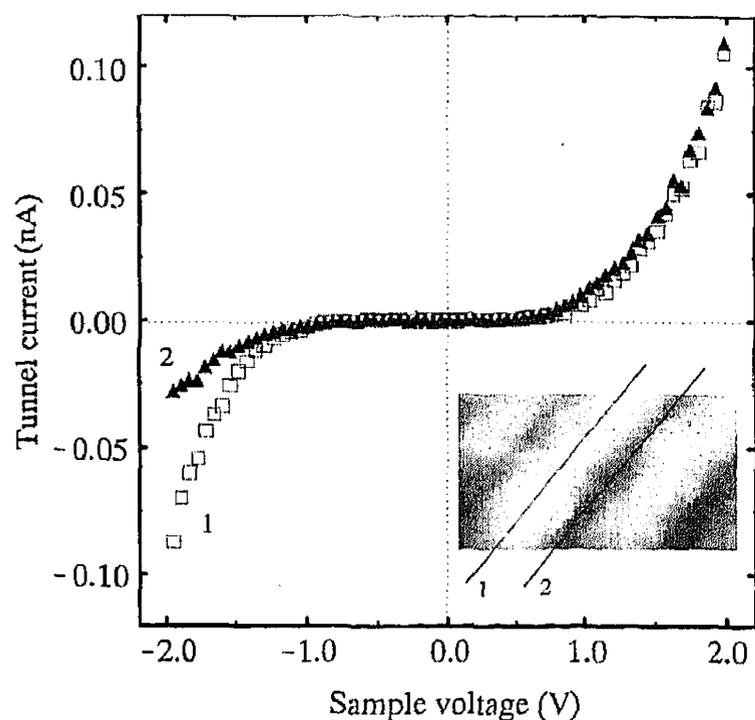


FIG. 3. I-V curves obtained with the tip positioned above a row (curve 1) and between two rows (curve 2). They were obtained in the areas indicated by line 1 and 2, respectively, in the simultaneously acquired $80 \times 40 \text{ \AA}^2$ constant-current image, shown in the inset. The tip-sample distance was set by stabilizing a 100 pA tunnel current at +2.0 V sample bias.

ment does not have much influence on the final surface structure as seen with STM, provided that it followed by annealing at sufficiently high temperatures. For the thin-film samples 850 K was, however, not high enough to produce a flat and regular surface, which requires temperatures up to 1200 K. This will, however, result in an even higher rate of Mg diffusion from the substrate, which was already significant. The relatively easy diffusion of the small Mg^{2+} ions into the Fe_3O_4 film is facilitated by the existence of the compound MgFe_2O_4 , which is isostructural to MgO and Fe_3O_4 . As the lattice mismatch between these compounds is only small, a coherent incorporation of MgFe_2O_4 is possible. We can, however, rule out that the complete film has been transformed into MgFe_2O_4 , since this is an insulator which obviously does not allow STM measurements. Although the formation of the row reconstruction observed with STM is hardly hindered by the replacement of Fe^{2+} with Mg^{2+} , for the magnetic properties this will certainly have more serious implications. For the use of Fe_3O_4 as test system for spin-sensitive STM this is of course an unsatisfactory situation, which might be improved by insertion of a diffusion barrier such as NiO between substrate and Fe_3O_4 .

The results of spatially resolved I-V spectroscopy have shown that the tunneling of electrons from the filled Fe_3O_4 states is a factor of 3 higher above a row than between two neighboring rows. This is consistent with the previously pro-

posed structure of the rows,¹² in which the oxygen content is higher and the tetrahedrally coordinated Fe^{3+} ions are absent. A locally larger amount of negatively charged O^{2-} ions in a row translates into a higher density of filled states, while a locally smaller content of positively charged Fe ions corresponds to a lower density of empty states above the Fermi level. Both contributions tend to increase the current at negative sample bias with respect to the current at positive bias, in agreement with the spectroscopic measurements presented in Fig. 3.

Summarizing, we have presented STM measurements on a MBE-grown thin Fe_3O_4 layer on MgO . Vacuum annealing this film at 850 K produced the onset of a row reconstruction of the same form as on bulk single crystals, despite the presence of significant amounts of Mg ions originating from the substrate. We succeeded in detecting local differences in the current-voltage characteristics, with a factor of 3 higher current of electrons tunneling from the Fe_3O_4 sample into the tip when positioned above a row. We believe that such local spectroscopic information is valuable for the determination of the nature of the row reconstruction.

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