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$Fe_3O_4(110)$–(1×3) revisited: Periodic (111) nanofacets

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ABSTRACT

The structure of the $Fe_3O_4(110)$–(1×3) surface was studied with scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and reflection high-energy electron diffraction (RHEED). The so-called one-dimensional reconstruction is characterized by bright rows that extend hundreds of nanometers in the $[\bar{1}10]$ direction and have a periodicity of 2.52 nm in [001] in STM. It is concluded that this reconstruction is the result of a periodic faceting to expose {111}-type planes with a lower surface energy.

Magnetite (Fe_3O_4) is a common material in the Earth's crust and plays an important role in geochemistry and corrosion [1,2]. At room temperature, Fe_3O_4 crystallizes in the inverse-spinel structure, and Fe cations occupy tetrahedrally (Fe_{tet}) and octahedrally (Fe_{oct}) coordinated interstices within a face-centered cubic lattice of O^{2-} anions. Natural single crystals are typically octahedrally shaped and expose {111} facets, consistent with density functional theory (DFT)-based calculations that find (111) to be the most stable low-index surface [3,4]. In recent years, however, advances in synthesis have allowed the size and shape of Fe_3O_4 nanomaterial to be tailored to enhance performance in applications such as groundwater remediation, biomedicine, and heterogeneous catalysis [1,5], and nanocubes and nanorods exposing {100} surfaces have been reported [6,7]. To date, there have been no reports of Fe_3O_4 nanomaterial exhibiting {110} surfaces.

In this light, it is perhaps unsurprising that the majority of studies aimed at uncovering the structure–function relationship of Fe_3O_4 surfaces have focused on the (111) and (100) facets [2,8,9]. Nevertheless, there have been a handful of experimental studies of single crystals cut in the (110) direction [10–12], and $Fe_3O_4(110)$ thin films have been successfully grown on MgO(110) [13–16]. In most situations, a (1×3) reconstruction has been reported. In STM, the (1×3) surface has been shown to exhibit an unusual appearance with bright rows that extend for hundreds of nanometers in the $[\bar{1}10]$ direction, and has been termed a 1-dimensional reconstruction. However, there is no reliable model for this surface structure. $Fe_3O_4(110)$ has also been studied by theoretical methods, but these investigations did not consider the reconstruction [17–22], instead focusing on a comparison of bulk-like surface terminations with a (1×1) unit cell. In this paper, we revisit the surface structure of $Fe_3O_4(110)$–(1×3) using STM, LEED, and RHEED experiments, and conclude that the "1D reconstruction" reported previously is the result of periodic faceting to expose the {111} planes, presumably due to their lower surface energy.

The STM experiments were performed in an ultrahigh vacuum (UHV) system with connected vessels for preparation and analysis, with base pressures of 1×10^{-10} mbar and 5×10^{-11} mbar, respectively. A natural $Fe_3O_4(110)$ single crystal (SurfaceNet GmbH) was prepared by cycles of 10 min sputtering (1 keV Ar^+ ions, $\approx 2\ \mu A/cm^2$) and subsequent annealing. The influence of the annealing temperature (varied between 400 and 900 °C) and environment (from UHV to an O_2 partial pressure of 10^{-6} mbar) were systematically studied. A summary of the surfaces prepared is available in the supplementary information. The 1D reconstruction observed previously by Jansen et al. [10] in STM images was omnipresent for all conditions, although the length of the 1D rows was maximized at 800 °C. XPS measurements were acquired with a non-monochromatized Al Kα source and a SPECS PHOIBOS 100 analyzer with a pass energy of 90 eV. Temperatures were measured with a K-type thermocouple spot-welded near the sample plate and are underestimated by ≈50 °C. STM measurements were conducted using an Omicron μ-STM with electrochemically etched W tips in constant current mode. STM images were corrected for creep of the piezo scanner [23].

The best-quality $Fe_3O_4(110)$–(1×3) LEED pattern (Fig. 1b) was obtained after annealing at 800 °C, consistent with the previous work of Jansen et al. [10]. The LEED spots are consistent with a periodicity of 0.3 nm and 2.5 nm in the $[\bar{1}10]$ and [001] direction, respectively. A second set of LEED spots suggestive of an additional 0.6 nm periodicity along $[\bar{1}10]$ direction are weakly visible, and we note that these spots

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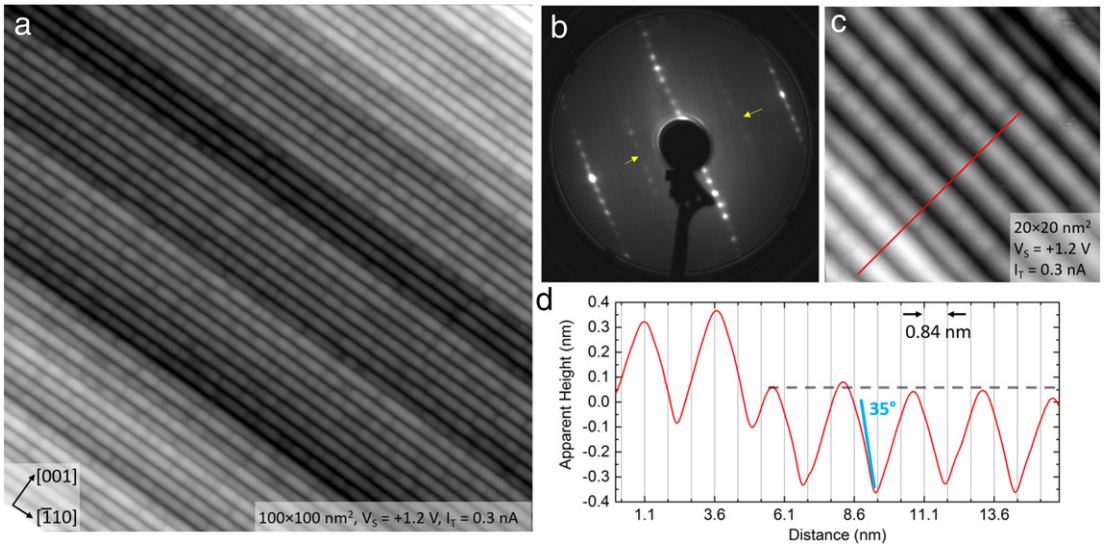

Fig. 1. STM images of the $Fe_3O_4(110)$ surface acquired after sputter/anneal cycles. (a) Overview image (100×100 nm^2, $V_S = +1.2$ V, $I_T = 0.3$ nA) showing bright rows that run in the [$\bar{1}$10] direction for hundreds of nm without break. Step edges have a height of 0.3 nm and are parallel to the rows. The periodicity in the [001] direction is 2.52 nm. (b) The (1×3) reconstruction observed in LEED. Weak spots due to an additional 0.6 nm periodicity are also visible and exhibit extinctions due to a glide symmetry (yellow arrows). (c) Small-area STM image (20×20 nm^2, $V_S = +1.2$ V, $I_T = 0.3$ nA) including a step in the bottom left of the image. (d) Line profile acquired from the position of the red line in (c). The grid lines in the plot correspond to 0.84 nm, i.e. one bulk unit cell. Each peak is separated by three grid lines, and the registry shifts by ½ of one unit cell between alternate layers. The maximum slope measured by STM is ≈35°, in agreement with the proposed {111} facet model, and the measured corrugation of the ridge-trough structure (0.46 nm) is greater than the step height (0.3 nm).

appeared stronger for lower annealing temperatures. STM images of the $Fe_3O_4(110)$ sample annealed at 800 °C reveal rows in the [$\bar{1}$10] direction (Fig. 1a), as observed previously by other groups [10,12]. In overview images (Fig. 1a), the rows extend over hundreds of nanometers without a break, and have a periodicity in the [001] direction of ≈2.52 nm (i.e. approximately three times the lattice parameter of 0.8396 nm). Steps on this surface have an apparent height of 0.3 nm, consistent with repeat distance of equivalent layers in the (110) direction (0.297 nm). At lower annealing temperatures (400–650 °C), the appearance of the surface is similar, but the rows feature more kinks and steps (see supplement, Fig. S1). At higher temperatures (900 °C) some missing sections appear in the rows (see supplement, Fig. S1).

Many attempts were made to image the (1×3) surface with atomic resolution while repeatedly preparing the sample, but no consistent structure was obtained. Indeed, it quickly became clear that such images were primarily dominated by the structure of the STM tip, because modification of the tip shape by Ar^+ sputtering and/or pre-scanning a clean Au(110) single crystal led to a different corrugation even on the same sample preparation. This experience suggests that the electronic corrugation along the rows is weak, while across the rows, the surface is "sharper" than the STM tip. Consequently, for analysis, we focus on the subset of images in which the corrugation across the rows is highest. One such image is shown in Fig 1c, together with a line profile in the [001] direction (Fig. 1d). The measured corrugation of the surface (which should be taken as a minimum value due to tip convolution effects [24]) is 0.46 nm, which is significantly larger than the distance between similar layers in the [110] direction (0.30 nm). Furthermore, the maximum slope angles measured are 30–35°, which is close to the angle of 35° expected between the (110) and (111) planes (blue line in Fig. 1d). Although not a direct measurement due to the convolution with tip shape [24], such a measurement does represent a minimum value for the real surface [25,26]. Over the course of many experiments, a value in excess of 35° was never observed. A line profile along the top of the ridge (See Fig. S2) reveals an irregular structure, although it is common that two intensity maxima are 0.6 nm apart. This periodicity corresponds to the very weak LEED spots in Fig 1b.

To investigate whether the (1×3) reconstruction might be related to the formation of {111} nanofacets, we performed RHEED experiments in a separate vacuum system (Fig. 2). The sample was prepared in the same way, and the presence of the (1×3) reconstruction was confirmed by in-situ LEED and STM (SPECS STM 150 Aarhus). Strong reflections were observed at an angle of 70° for all electron energies between 15 and 30 keV when the incident beam was aligned parallel to the [$\bar{1}$10] direction. This is the specular direction for {111} facets ($70° = 2 \times 35°$). The high density of spots on the Laue circle of the RHEED images is related to the (1×3) superstructure. The large (2.52 nm) periodicity of this reconstruction results in many closely spaced spots that vary in intensity with electron energy.

On the basis of the experimental results shown in Figs. 1 and 2, we propose a model of the $Fe_3O_4(110)$ surface based on {111} nanofacets. One possible realisation of such a structure is presented as Fig. 3 (green atoms are Fe_{tet}, blue atoms are Fe_{oct}, O is red). At the apex of the structure there is a row of Fe_{oct} atoms, together with their neighboring O atoms. In this respect, our model is similar to that of Jansen et al. [10], who observed a 3 Å periodicity along the top of the rows with STM. Indeed, with an idealized STM tip one would expect to image the Fe_{oct} atoms as a row of protrusions in empty-states images as they have density of states near E_F, and this is regularly achieved on the $Fe_3O_4(100)$ surface. However, as mentioned above, we were unable to image this structure reproducibly despite repeated attempts, most likely due to the convolution of the surface structure with the tip morphology. Nevertheless, the structure is consistent with the (1×3) periodicity observed in LEED, and sometimes weakly observed in Fourier transforms of STM images. Note that O atoms are not typically imaged on Fe_3O_4 surfaces as they have little density of states in the vicinity of E_F [8], and Fe_{tet} have DOS at approximately 2 eV below E_F [27]. STM images of the surface in filled states are also dominated by the ridge-trough structure and are indistinguishable from those in empty states.

Where our model differs from that of Jansen et al. [10] is that they propose that the trough contains the subsequent Fe_{oct}–Fe_{tet}–O containing layer, and that the driving force for reconstruction is related to stoichiometry. We, on the other hand, propose the driving force for reconstruction is anisotropy in the surface free energy. Such considerations drive faceting on open metal surfaces [28–30], where the exposure of close-packed surfaces is energetically favorable. On metal oxides, faceting has been observed for rocksalt compounds such as NiO(100) [31] and MnO [32],