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A metastable Fe(A) termination at the $Fe_3O_4(001)$ surface

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ABSTRACT

A metastable Fe(A) terminated Fe₃O₄(001) surface was prepared by tailoring the surface preparation conditions. STM, LEIS and LEED are utilized to demonstrate that annealing the Ar⁺ sputtered surface to 350 °C produces an Fe(A) terminated surface with a ($\sqrt{2} \times \sqrt{2}$)R45° superstructure. Within the superstructure both single Fe atoms and Fe dimer species are observed. The surface is reoxidized upon annealing to higher temperatures, eventually leading to the recovery of the energetically favorable Jahn–Teller distorted surface at 700 °C. The ability to reproducibly prepare the Fe(A) termination in this simple manner will allow investigations into the structure–function relationship for this important technological material.

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Magnetite (Fe₃O₄) is a naturally abundant oxide material in the environment and consequently its surfaces play an important role in environmental redox reactions, corrosion processes, and geochemistry. Moreover, Fe₃O₄ is utilized in many industrial applications where surface properties are critical including catalysis [1,2] and groundwater remediation [3]. The fact that Fe₃O₄ is a room temperature half-metal [4] has led to attempts to incorporate it as a ferromagnetic electrode in spintronics devices, but the performance of device prototypes has been disappointing [5–7] due to the ill-defined nature of the Fe₃O₄/ semiconductor interface [8,9].

In the bulk, Fe₃O₄ crystallizes in the inverse-spinel structure with Fe^{3+} cations in tetrahedral sites and a 1:1 mixture of Fe^{2+} and Fe^{3+} in octahedral sites (see Fig. 1a). For the polar (001) surface, early studies considered structural models that were auto-compensated and consistent with the $(\sqrt{2} \times \sqrt{2})$ R45° symmetry observed in low energy electron diffraction (LEED), i.e. terminated by either 1/2 ML Fe(A) atoms (Fig. 1c) [10–12] or a Fe(B) layer with one oxygen vacancy per unit cell [12,13]. However, density functional theory (DFT) calculations [14] combined with LEED I-V measurements have shown that a Jahn–Teller distorted Fe(B) termination (B-termination), with a full complement of oxygen atoms (Fig. 1b), is the most stable surface across a wide range of chemical potentials. This model is consistent with the undulating rows of Fe(B) atoms observed in scanning tunneling microscopy (STM) images [11,13,15–17]. DFT calculations also predict that charge ordering occurs with the B-termination, inducing a bandgap of ~0.3 eV in the surface layers [18-20]; a prediction later confirmed by scanning tunneling spectroscopy (STS) measurements [20]. However, experimental [21,22] and theoretical studies [23,24] continue to propose Fe(A) terminations [14,18]. Experimentally, STM images of $Fe_3O_4(001)$ thin films grown in an Fe rich environment (on an Fe(001) buffer layer) appear to exhibit Fe dimer species [25] (see Fig. 1d) similar to those originally proposed by Rustad et al. [26] on the basis of molecular dynamics simulations. Interestingly, this surface exhibits a modified valence band structure compared to the B-termination [27].

Understanding factors that govern the surface terminations of Fe_3O_4 is critical for the reliable interpretation of catalytic properties and attempts to modify the interfacial electronic structure for spintronics devices. In this letter we utilize STM, low energy ion scattering (LEIS) and LEED to show that both the B-termination and a metastable Fe(A)termination can be reproducibly prepared within one sputter/anneal cycle through variation of the annealing temperature. This discovery will allow direct comparison of the structure–function relationship of this important technological material.

The experiments described here were conducted on a synthetic $Fe_3O_4(001)$ sample grown using the floating zone method by Prof. Z. Mao and coworkers at Tulane University. The sample was oriented, cut and polished by MaTeck GmbH. All STM experiments were conducted in an ultra high vacuum (UHV) system comprising separate vessels for sample preparation (base pressure 1×10^{-10} mbar) and analysis (base pressure 5×10^{-11} mbar). The preparation chamber allows for *in situ* sample cleaning via Ar⁺ sputtering and annealing by electron beam bombardment at the backside of the Mo sample plate. The analysis chamber provides facilities for LEED, X-ray photoelectron spectroscopy (XPS), and STM (SPECS), in which electrochemically etched W tips were used.

The LEIS experiments were conducted in a separate vacuum system (base pressure 5×10^{-11} mbar) and utilized a rastered 1 keV



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Fig. 1. (a) The inverse spinel Fe₃O₄ bulk unit cell containing O (red), tetrahedral Fe(A) atoms (cyan) and octahedral Fe(B) atoms (yellow). (b) Perspective view of the Jahn–Teller distorted B-termination of Fe₃O₄(001) [14]. The Fe(A)_{NARROW} site (see text) is indicated by the blue oval. (c) Top view of the 1/2 ML Fe(A) termination. The terminal Fe(A) atom (blue) is in the Fe(A)_{NARROW} site. The $(\sqrt{2} \times \sqrt{2})$ R45° surface unit cell is indicated in black. (d) Top view of the proposed Fe-dimer termination of Fe₃O₄(001), with the dimer (blue) situated above a subsurface Fe(A) vacancy [25]. (e) Top view of the Fe-dimer termination proposed in this work where the dimer lies symmetrically about the Fe(A)_{NARROW} site.

He⁺ beam of \approx 70 nA. The LEIS data were acquired following a beam damage assessment, in which a reduction in the O peak intensity was observed after several repeat measurements due to preferential sputtering. Consequently, LEIS data were acquired using data acquisition times well below that required to damage the surface (three scans are averaged in each dataset).

In Fig. 2 we show STM images of the Fe₃O₄(001) surface acquired following Ar⁺ sputtering (1 keV, 15 min, $I_s \sim 1 \mu A$) and subsequent annealing in UHV to 350 °C, 500 °C and 700 °C. The image acquired after 700 °C (Fig. 2a) annealing resolves the undulating rows of the B-termination, as observed previously (see Fig. 1(b)) [13,15,16], and two typical surface defects are highlighted within the image. Firstly, double protrusions over the Fe(B) rows (pink arrows, pointing left) are due to surface hydroxyl species [15]. Secondly, there exist single bright protrusions between the Fe(B) rows in Fe(A) bulk continuation sites (blue arrow facing right). It is important to note that the relaxation of the Fe(B) atoms within the B-termination renders the two surface Fe(A) sites inequivalent. One site, Fe(A)_{NARROW}, is located where the Fe(B) rows come together (blue oval in Figs. 2a and 1b), while the $Fe(A)_{WIDF}$ site is located where the Fe(B) rows are further apart (yellow oval in Fig. 2a). In our STM images we always observe isolated Fe(A) defects to appear in the $Fe(A)_{NARROW}$ site.

Annealing the sputtered surface to 500 °C (Fig. 2b) leads to an increase in the number of observed Fe(A) atoms. The undulating rows of the B-termination remain visible, and it is clear that the surface Fe(A) atoms continue to occupy the $Fe(A)_{NARROW}$ site. Note that saturation coverage of Fe(A) atoms occupying only the $Fe(A)_{NARROW}$ site would give the 1/2 ML Fe(A) model presented in Fig. 1c. Annealing the sputtered surface to 350 °C (Fig. 2c) produces a surface where the B-termination is no longer visible. In its place we observe protrusions with a $(\sqrt{2} \times \sqrt{2})$ R45° periodicity, however, closer investigation of the protrusions reveals two distinct types. The blue oval (solid line) in Fig. 2c highlights a region where the protrusions are all of similar intensity. In contrast, in the yellow oval (dashed) we additionally observe several larger, brighter protrusions. In the highest resolution images (Fig. 2d) we are able to resolve the bright protrusions as a dimeric species separated by ~0.3 nm, as evidenced by the line profile presented in Fig. 2e. The $(\sqrt{2} \times \sqrt{2})$ R45° LEED pattern observed for the 350 °C annealed surface is somewhat weaker than that observed for the B-termination, most likely because the surface has smaller terraces and less long range order as a result the sputtering process.

Fig. 3 shows experimental data obtained from LEIS experiments conducted for the 700 °C annealed (B-termination; black curve) and 350 °C annealed (Fe(A) termination; red curve) surfaces. For both surface preparations peaks are observed at 455 eV and 812 eV due to elastic scattering from surface O and Fe atoms, respectively. However, the integral of the Fe peak at 350 °C is ~50% larger than for the 700 °C surface, while the O peak is marginally reduced. These data suggest that the protrusions observed in the Fe(A)_{NARROW} sites in STM are due to Fe atoms.

Overall the experimental data presented in this letter demonstrate that both the B-termination and a metastable Fe(A) termination can be formed at the Fe₃O₄(001) surface within one sputter-anneal cycle through variation of the annealing temperature. Merely annealing the B-termination at 350 °C induces no change to the surface observed in STM images (data not shown), therefore we conclude that Ar⁺ sputtering is the critical process driving the formation of the Fe(A) termination. TRIM [28] simulations of the sputtering process indicate that O is preferentially sputtered by a factor of approximately × 2.5 for our preparation conditions, leading to a surface with an excess of Fe. Both STM images and the LEED pattern obtained after sputtering are indicative of a disordered, roughened surface (data not shown).

Once a non-stoichiometry at the surface is established, the annealing temperature controls the ultimate surface termination. However, two distinct processes are at work. 350 °C annealing is sufficient to facilitate significant surface diffusion, leading to the formation of flat, well-ordered terraces, but the non-stoichiometry remains. Significant surface-bulk diffusion only occurs at higher temperatures, evidenced by the reoxidation of the surface with increasing temperature. Finally, at 700 °C, the B-termination is recovered.

Interestingly, the STM images acquired following 350 °C annealing show that the Fe terminated surface comprises both Fe dimers and single Fe atoms within the same ($\sqrt{2} \times \sqrt{2}$)R45° superstructure. This suggests that both species reside at the same site within the surface reconstruction; i.e., the Fe(A)_{NARROW} site (see Fig. 1(c) and (e)), in contrast to prior molecular dynamics calculations [26], which found that Fe dimers occupy a site above a subsurface Fe(A) vacancy (Fig. 1(d)).

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Fig. 2. (a) $11 \times 11 \text{ nm}^2$ STM image (1.2 V, 0.3 nA) acquired after 1 keV Ar⁺ sputtering for 15 min and annealing to 700 °C, indicating the Fe(A)_{NARROW} (blue oval) and Fe(A)_{WIDE} (yellow oval) sites. Blue arrows (facing right) indicate protrusions at Fe(A)_{NARROW} sites. Pink arrows (facing right) indicate hydroxyl species [15]. (b) $11 \times 11 \text{ nm}^2$ STM image (1 V, 0.3 nA) acquired after 1 keV Ar⁺ sputtering for 15 min and annealing to 500 °C. Blue arrows (facing right) indicate protrusions at Fe(A)_{NARROW} sites. (c) $11 \times 11 \text{ nm}^2$ STM image (1 V, 0.24 nA) acquired after 1 keV Ar⁺ sputtering for 15 min and annealing to 350 °C. The blue oval (solid line) in the 350 °C image encloses a region with single Fe(A) atoms with a ($\sqrt{2} \times \sqrt{2}$)R45° superstructure. The yellow oval (dashed) indicates a region where two distinct size and brightness of Fe(A) protrusion are observed due to Fe dimerization. (d) 2.88 × 1.68 nm² STM image (1 V, 0.27 nA) showing Fe(A) dimers following 30 min sputtering and 350 °C UHV annealing. (e) Line scan associated with the pink line in (d). Each STM image contains the complementary ($\sqrt{2} \times \sqrt{2}$)R45° LEED pattern acquired at 90 eV from the same surface as an inset.

In the past, charge compensation arguments have been invoked in the discussion of the $Fe_3O_4(001)$ surface termination [12,13,29]. Under this framework and assuming nominal bulk charges, either



Fig. 3. LEIS data (1 keV He⁺, \approx 70 nA, scattering angle: 120°) acquired from the Fe₃O₄(001) surface following Ar⁺ sputtering and 700 °C (black) and 350 °C (red) annealing.

oxygen vacancies or 1/2 ML Fe are required to stabilize the surface polarity [13,29]. For the B-termination however, DFT calculations [14,30] have shown that the surface is stabilized through a symmetry-lowering lattice distortion, and that the charges of the surface atoms are *not* the same as in the bulk.

To date, all models for an Fe(A) terminated surface have contained 1/2 ML Fe atoms, in line with the charge compensation criterion. Chambers et al. [29] proposed a 1/2 ML Fe(A) termination, consistent with the observed $(\sqrt{2} \times \sqrt{2})$ R45° symmetry (see Fig. 1(c)). Later the dimer model proposed by Rustad et al. [26] predicted the existence of surface Fe dimers in a $(\sqrt{2} \times \sqrt{2})$ R45° superlattice (Fig. 1d), but one half of the dimer came about through migration of a subsurface Fe(A) to the surface layer, thus maintaining the charge-compensated surface layer. Most recently, Spiridis et al. observed Fe dimers experimentally in STM [25], but found that, on average, the excess Fe coverage was 1/2 ML, satisfying global charge compensation. However, since Fe₃O₄ has significant conductivity (that of a poor metal) it is not clear that the "polarity catastrophe" [31] would occur in this material. Our STM data demonstrate that Fe coverages well in excess of 1/2 ML are stable on the Fe₃O₄(001) surface. Furthermore, integration of the Fe peaks in the LEIS data (Fig. 3) suggests that an average coverage closer to 1 ML can be achieved (i.e., two Fe atoms in 1/2 of the Fe(A) bulk continuation sites). Therefore, we conclude that charge compensation arguments based on nominal bulk charges are unreliable for predicting the surface structure of magnetite.

The ability to quickly and reproducibly form an Fe(A) termination at the Fe₃O₄(001) surface will facilitate direct comparison of the reactivity and electronic properties with the B-termination. For example, the B-termination exhibits a band gap, which could be linked to the poor magnetoresistance measured for Fe₃O₄-based spintronic device prototypes. Population of the surface with undercoordinated Fe atoms could result in (half) metallization of the surface, as was recently observed after saturation adsorption of atomic H [15,32]. In addition, under coordinated cation sites are often active sites for the dissociation of molecules, for example on the Fe₃O₄(111) surface [33], and therefore the Fe(A) termination is likely to be more reactive than the relatively inert B-termination.

In this letter we have shown that a metastable Fe(A) termination of the Fe₃O₄(001) surface can be created by a single cycle of Ar⁺ sputtering and annealing at 350 °C. The structure arises through the ordering of excess Fe, created through preferential sputtering of surface O. Annealing the sample to higher temperatures leads to the re-oxidation and the recovery of the B-termination. The ability to reproducibly prepare the Fe(A) termination will allow details of the structure–property relationship of Fe₃O₄ surfaces to be studied, and may have important implications for the use of Fe₃O₄ in catalysis and spintronics applications.

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