



Impurity stabilized near-surface phase on ion bombarded α -Fe₂O₃(0001)

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Abstract

Following Ar⁺ ion bombardment, an epitaxial spinel phase forms on the near-surface of hematite specimens that contain impurity species. This near-surface spinel phase can readily be distinguished in a transmission electron diffraction pattern, and is stable under a much broader range of oxygen partial pressures than has been previously observed in the literature. Conversely, hematite samples which are impurity free show no evidence of an epitaxial spinel phase. Regardless of the impurity concentration, samples annealed at high temperature in oxygen-rich environments show (1 × 1) diffraction patterns indicative of a bulk hematite termination.

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1. Introduction

The mineral hematite (α -Fe₂O₃) has received much attention in recent years due to the rich and varied reconstructions that form on its surface following argon ion (Ar⁺) bombardment and

annealing treatments. Previous studies have reported iron or oxygen terminated (1 × 1), Fe₃O₄, and so-called bi-phase selvages on the (0001) surface of hematite after annealing in the appropriate combination of temperature and oxygen partial pressure [1–4]. In all cases, these studies used mineralogical or thin film samples that were sputtered via argon ion bombardment prior to annealing. Ar⁺ ion bombardment is a common technique used in the surface science community

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to ensure the cleanliness of surfaces prior to study, and it is well documented that this method is destructive and causes drastic changes in surface stoichiometry [5,6]. In fact, it is exactly because Ar^+ ions are destructive at high energies that they are commonly used to thin transmission electron microscopy (TEM) samples of materials such as hematite that do not lend themselves to thinning via common electropolishing methods.

In this study, we have chosen to use primarily TEM along with various spectroscopic techniques in order to probe the nature of the Ar^+ ion milled (0001) surface of hematite. We will show that argon ion bombardment serves as an empirical test that correlates with the purity of hematite samples.

2. Experimental

Single crystalline (0001) oriented hematite substrates were obtained from various sources. Blocky massive mineralogical samples with naturally occurring specular faces (origin China, Brazil, Africa, and Russia) were obtained from Commercial Crystal Laboratories, Inc., Naples, FL. The samples were purchased as $10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$ (0001) oriented wafers. Mineralogical “iron rose” samples (hereafter referred to as rosettes), which exist naturally as thin (0001) oriented platelets, were obtained from Ouro Preto Minas Gerais, Brazil. Synthetic hematite crystals were grown using the optical floating zone furnace in the traveling solvent zone configuration [7] and were sliced into thin (0001) wafers.

All samples were prepared using standard TEM preparation methodologies for oxide single crystals. The wafers (or natural platelets) were first cut into 3 mm (TEM size) disks using a South Bay Technology circular disk cutter with a brass tip and 600 grit SiC slurry. The resulting $3\text{ mm} \varnothing \times \sim 0.5\text{ mm}$ thick disks were then thinned to approximately $100\text{ }\mu\text{m}$ using abrasive SiC paper and then mechanically dimpled to between 5 and $15\text{ }\mu\text{m}$ in the center using a Gatan dimpler. Following dimpling, the samples were polished optically flat using $0.05\text{ }\mu\text{m}$ alumina paste and cleaned thoroughly in an ultrasonic cleaner for several minutes.

All samples were thinned to electron transparency using a Gatan Precision Ion Polishing System (PIPS) with Ar^+ ions operated at 5 kV and 15–30 mA milling current. Typical milling times range from 2 to 4 h depending on the initial thickness of the dimpled samples.

TEM analysis, used in order to determine the phase(s) present on the surface of the ion milled hematite samples, was performed on either a Hitachi H-8100 TEM operated at 200 keV or a Hitachi UHV-H9000 HRTEM operated at 300 keV. Each microscope was equipped with a double tilt stage.

Impurity analysis was performed using one or several of the following methods: inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed using a Thermo Jarrell Ash Atomscan Model 25 Sequential ICP Spectrometer and inductively coupled plasma-mass spectroscopy (ICP-MS) was performed on a VG PQ ExCell Spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on TEM-ready samples using a Physical Electronics hemispherical energy analyzer with an aluminum anode X-ray source. Finally, X-ray fluorescence was performed on a Bruker S4 Explorer. For the XRF measurements, Na was neglected and the remaining elements were normalized to 100%.

3. Results

3.1. Impurity analysis

Impurity analysis was performed on over 20 different hematite specimens using the methodologies mentioned above (see Table 1). Not every crystal was tested using every methodology available; instead each crystal was tested for purity in at least one way. In these experiments, we were not concerned with obtaining the *exact* impurity profile of each sample but rather needed to know if any impurities could be detected by common means and if so, what were the major contaminating species. Each mineralogical sample except for R1 contained at least some impurity and it was found that the actual atomic species present and their relative amounts varied drastically from sample to sample.

Table 1

Representative list of hematite samples tested, their major impurities, and the method used to test them

Sample	Sample type	Major impurities	Approx. impurity	Method(s)
S1	Specular mineral	Mg, Al, Cr, Cd	5 wt.%	ICP-MS, XPS
S2	Specular mineral	Cr	0.5 wt.%	XRF
R1	Rosette mineral	–	No peaks	XPS
R2	Rosette mineral	Ti, Ca	4 wt.%	XRF, XPS
SY1	Synthetic	Ca	0.20 at.%	ICP-AES
SY2	Synthetic	–	0.00 at.%	ICP-AES, XRF

This is a partial list of the over 20 total samples examined.

On average, the specular hematite samples proved to be the most contaminated, with the most variation in contaminants. Impurity concentrations of these samples ranged from 0.5 wt.% up to >10 wt.% with an average of approximately 2 wt.%. In all we examined the chemical composition of over 15 different samples of this type, primarily by XRF and XPS. XRF was chosen because it is a quick, easy, non-invasive test that does not require UHV and can be quantitative (although there are large errors associated with this technique). In Table 1, we have included data from two representative samples of this group of over 15. The hematite rosette samples proved to be cleaner, on average, than the blocky massive crystals. In fact, the several TEM samples of rosette “R1” examined did not show any contamination peaks in the XPS spectrum and appear to be quite pure.

Finally, we tested the purity of two synthetic hematite single crystals grown in an optical floating zone furnace in the traveling solvent zone configuration. These crystals were grown using a CaFe_4O_7 -based solvent under 8 bars of O_2 [7]. The starting material for the two samples consisted of 99.998% pure hematite powder (Alfa Aesar) for SY1 and 99.999% pure CaCO_3 powder (Alfa Aesar) for SY2. The Ca content of the grown single crystals was tested via ICP-AES. The first of these (SY1) contained Ca:Fe of 0.005 (0.2 at% of Ca) and the second (SY2) contained no contamination that could be detected by ICP-AES or XRF.

3.2. TEM results: impure hematite samples

After Ar^+ ion bombardment, hematite samples that contain impurities detectible with either

XRF, XPS, ICP-AES and ICP-MS exhibit a ferrite spinel-type phase near the surface, which is detected via transmission electron diffraction. From the diffraction patterns, it is evident that this spinel phase forms epitaxially on the hematite ‘substrate’ and is rotated 30° with respect to the hematite surface unit cell (Fig. 1). When these samples are annealed in a flow of oxygen at 830–930 °C for 2.0–2.5 h, the spinel phase is oxidized and only the hematite (1×1) pattern is left (Fig. 2).

The exact space group of the spinel near-surface phase can not be known from a single diffraction experiment in this orientation. It is possible that the spinel phase can be indexed to any number of spinel or spinel-like space groups. For example,

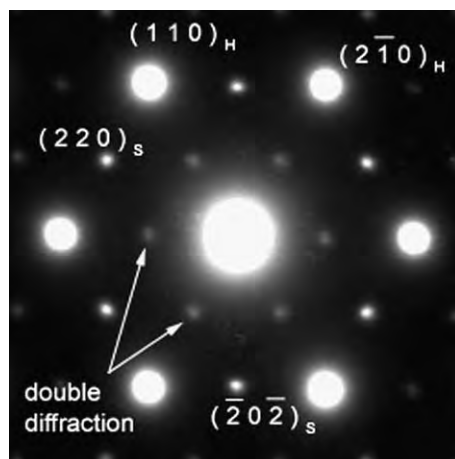


Fig. 1. Transmission electron diffraction pattern from an Ar^+ ion milled hematite single crystal (blocky massive type) containing impurity species. In addition to the first allowed spots of the corundum structure, extra spots from the spinel phase and those arising from double diffraction can be seen.

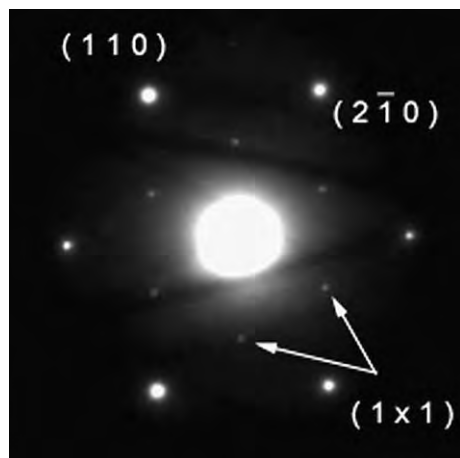


Fig. 2. Transmission electron diffraction pattern from a hematite single crystal containing impurity species after annealing in a flow of oxygen for 2 h. The spots from the spinel phase are no longer present and only the first allowed $\{110\}$ -type spots for the corundum structure are present. Faint Kikuchi lines can be seen indicating the diffraction pattern is taken from a relatively thick area.

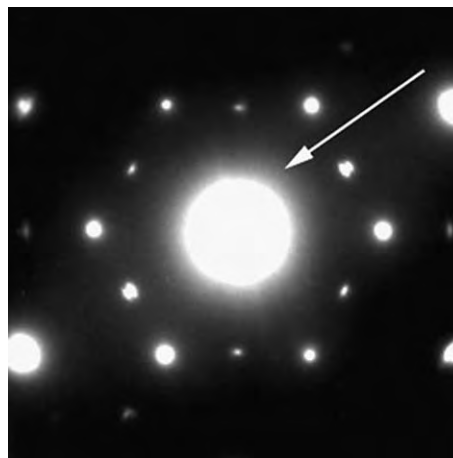


Fig. 3. Off-zone diffraction pattern for an ion-milled single crystal of hematite containing impurity species. Note the absence of diffraction spot (arrow) arising from double diffraction thus proving the spinel is Fe_3O_4 -type. Note that a tilting experiment of this type also rules out the presence of a surface reconstruction.

all of the spots present in the pattern can be indexed to a defect spinel space group ($p4_132$). Alternatively, all of the spots can be indexed to an inverse spinel-type space group ($fd3m$) if double diffraction is taken into account. In order to determine which type of spinel phase is present on the surface of the impure hematite samples, and to rule out the presence of a hematite surface reconstruction, a test for double diffraction was performed as outlined in [8]. If a specimen is carefully tilted far off ($\sim 10^\circ$) the zone axis to a more kinematical diffraction condition, any spots arising from double diffraction will decrease in intensity or disappear altogether. This test was performed on the impure hematite samples (Fig. 3) and the spots suspected of arising from double diffraction were no longer visible on the pattern once tilted off the zone axis, thus proving that the spinel-like phase on the surface is similar in structure to Fe_3O_4 (magnetite, an inverse spinel of $fd3m$ type, with $\{220\}$ spots present along with those arising from double diffraction). A tilting experiment of this kind also proves that the spinel phase is in fact a near-surface phase and not a reconstruction of hematite, as spots arising from

a surface reconstruction grow *more intense relative to the bulk* when the sample is tilted off the zone axis [9] due to the truncation of bulk rel-rods in reciprocal space (see Section 4).

From the transmission electron diffraction patterns it is obvious that the out of plane epitaxial relationship between the hematite (corundum) substrate and the ferrite spinel overlayer is that of $\{111\}_S \parallel \{0001\}_H$. The in-plane epitaxial relationship is impossible to determine unambiguously from this single diffraction experiment, but we believe based on the orientation relationship displayed in the diffraction and previous studies [10] it is likely $\{110\}_S \parallel \{100\}_H$.

3.3. TEM results: pure hematite samples

After Ar^+ ion bombardment, nominally pure hematite samples (S2, R1) do not show any evidence in the transmission electron diffraction pattern of a near-surface phase (Fig. 4). In fact, the ion milled TED patterns of these samples show only bulk-allowed spots for the corundum structure (space group #167, R-3c). Similar to the case of the impure samples, after annealing in a flow of

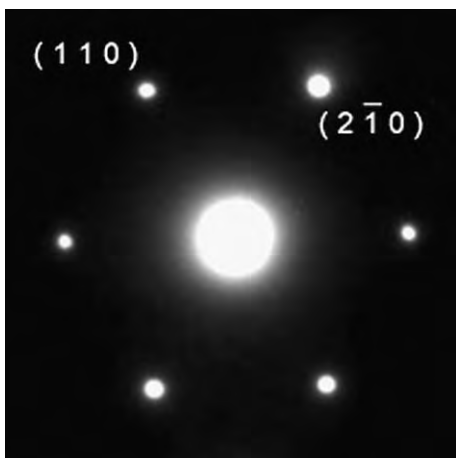


Fig. 4. Transmission electron diffraction pattern from a pure Ar^+ ion milled hematite specimen. Only the first allowed $\{110\}$ -type spots for the corundum structure are present.

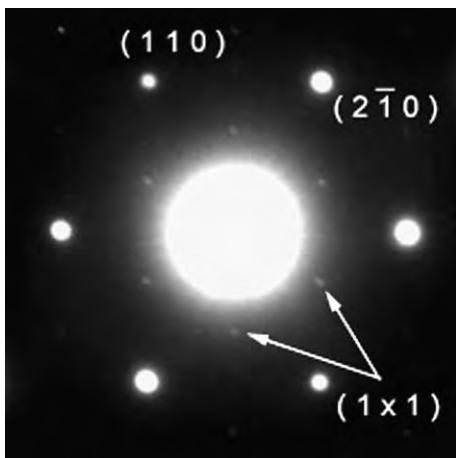


Fig. 5. Transmission electron diffraction pattern from a pure hematite sample after annealing in a flow of oxygen at $830\text{ }^\circ\text{C}$ for 2 h. The (1×1) spots can now be seen.

oxygen at $830\text{--}930\text{ }^\circ\text{C}$ for 2.0–2.5 h the hematite (1×1) pattern is left (Fig. 5).

4. Discussion

It is well known that Ar^+ ion bombardment drastically modifies the surface stoichiometry of oxide samples and that significant disorder and

reduction can occur. Previous studies [11] [1] which examined the ion bombarded surface of hematite using LEED and XPS found significant contribution to the Fe2p peaks from Fe^{2+} in the XPS spectra and absence of an LEED pattern after only 50 s of milling at 1 kV [12]. Another study using conversion-electron Mössbauer spectroscopy and small angle X-ray diffraction [13] found that $\alpha\text{-Fe}_2\text{O}_3$ reduced readily to sub oxides (Fe_3O_4 and FeO) following bombardment in doses of 1.0×10^{16} ions/ cm^2 and above.

The disadvantage to using LEED for this type of work is that it cannot penetrate past the disordered surface layer to “see” any crystalline phases which may lie below. In contrast, the TEM is uniquely suited to this type of study by virtue of the transmission geometry which can penetrate through the entire depth of the specimen. If a crystalline near-surface phase is present which lies beneath a disordered outer layer, hidden from the LEED probe, it will nonetheless be present in the transmission electron diffraction pattern.

Therefore, based on the previous studies of this system and our own results, we believe the morphology of these ion milled surfaces to be the following: all samples, whether or not they contain impurities, are covered in a disordered layer following Ar^+ ion bombardment in which there is some fraction of the original Fe^{3+} reduced to Fe^{2+} and even Fe^0 . Further, we believe that impure samples have an epitaxial ferrite spinel layer lying beneath this disordered layer. In contrast, the pure hematite samples do not have the ferrite spinel phase and are simply disordered and reduced on the surface.

The idea of having a spinel layer present (as opposed to a surface reconstruction of hematite) agrees well with the intensity ordering of the spots observed. More specifically, the $\{220\}$ spinel spots in Fig. 1 are quite bright and the double diffraction spots are slightly weaker than those, which is consistent with the fact that it is a surface phase with double diffraction and not a reconstruction. In a transmission electron diffraction pattern, spots arising from a surface reconstruction are typically four orders of magnitude weaker than bulk spots. If the spots in this pattern had come from a surface reconstruction, the intensity of the spots would be

much reduced. Furthermore, due to the truncation of bulk rel-rods and elongation of surface rel-rods in reciprocal space, any spots arising from a surface reconstruction become *stronger* when the specimen is tilted off of the zone axis [9]. This is in direct contradiction to our observations (Fig. 3) where as the samples are tilted, the spots arising from double diffraction disappear entirely. The above analysis is also consistent with the interpretation of similar LEED patterns on hematite surfaces seen in [1,3,14,15].

Upon annealing in an oxygen-rich environment all samples, regardless of their impurity content, show (1×1) diffraction spots characteristic of a bulk-truncated hematite surface. XPS spectra of impure annealed hematite samples show the persistence of the impurity species indicating that they did not appreciably diffuse away from the surface. The XPS spectra also indicate that there is no significant surface segregation of impurity species upon annealing. This indicates that under the present annealing conditions, hematite is the stable phase and can accommodate these impurities in its structure as point defects [14,16,17].

The stoichiometry of spinel (AB_2O_4) and inverse spinel ($B(AB)O_4$ —generally $(A_{1-x}B_x)(A_xB_{2-y})O_4$) materials is such that they have a higher cation to anion ratio than a given corundum material containing the same constituents. For example in the case of iron and oxygen containing compounds, the Fe:O ratio in hematite is 0.66 while the ratio in magnetite is 0.75. Charge neutrality in a spinel is accommodated by a reduction of the cation oxidation state. In the case of the inverse spinel Fe_3O_4 , charge neutrality is maintained when some of the iron on the octahedral sites exists in the Fe^{2+} oxidation state. Therefore, to reduce Fe_2O_3 to a spinel, there needs to be a net loss of oxygen and a compensating reduction of Fe^{3+} to Fe^{2+} .

This loss of oxygen and reduction to Fe^{2+} could also be achieved by the incorporation of impurity species into the hematite lattice, which must be accompanied by a charge-compensating lattice defect in order to maintain overall charge neutrality of the crystal. For example, the substitution of a higher valent ion for Fe^{3+} can lead to a reduction to Fe^{2+} whereas the substitution of a lower valent ion can lead to a charge compensating oxygen ion

vacancy. In fact, this has been shown experimentally in a study by Park and Kim [16].

Our results indicate that the impurity species found in hematite along with their charge neutrality maintaining defects must accelerate or stabilize the formation of a ferrite spinel upon *further* reduction via Ar^+ ion bombardment. In other words, it is not hard to form a ferrite spinel from hematite when many of the “ingredients” (including oxygen deficiency, and Fe^{2+} , or even in some cases a “B” cation) are already present. This is not surprising when it is considered that many of the common impurity elements found in hematite crystals readily form stable ferrite spinel compounds on their own. For example, the spinel group contains compounds such as magnesioferrite (Fe_2MgO_4), ulvospinel (Fe_2TiO_4), franklinite ($(Zn, Fe, Mn)(Fe, Mn)_2O_4$), chromite ($FeCr_2O_4$), and a host of others containing iron along with V, Al, Ge, Ni, Co, and Cu.

It must be stated that oxygen deficiency and presence of Fe^{2+} , while possibly necessary, are not a sufficient condition to form a stable crystalline spinel phase upon ion milling. If that was the case, then the epitaxial layer would also show up on the surface of the pure hematite samples where we argue that there is also reduction to Fe^{2+} and loss of oxygen (although to a much lesser extent). This points to the fact that either the impurity species themselves play a role in the stabilization of the spinel phase, or that when they are present their associated charge compensating defects are present in numbers much higher than one could get from ion milling alone.

Interestingly, the formation of the ferrite spinel phase does not depend on the type of contaminant present in the samples—it does not appear necessary to have a “spinel-forming” element present in the sample. We attribute this again to the fact that practically any type of impurity must have an associated charge compensating defect (oxygen vacancy or reduction of Fe^{3+} to Fe^{2+}). A good example of this is SY1 which contains only calcium which itself is not normally thought of as a spinel-forming element but nevertheless helped to stabilize the spinel phase.

The above result points to an interesting observation: it appears that the relative amount of

impurity has no effect on the formation of the spinel phase, at least in the quantities that we have measured empirically. As mentioned above for sample SY1, the presence of even 0.2 at.% Ca was enough to stabilize the formation of the spinel near-surface phase. While it maybe true that the cutoff for impurity concentration will vary from element to element, our experiments have shown that even a very small amount of impurity species is enough to stabilize the formation of the spinel near surface phase.

5. Conclusion

Argon ion bombardment and transmission electron microscopy may be used as a qualitative test for the purity of hematite single crystal specimens. Samples which contain impurity species will reduce when ion milled, forming a stable epitaxial layer of spinel underneath the disordered layer. This spinel layer can be readily observed in the transmission electron diffraction pattern, and is stable under a broader range of oxygen partial pressures than have been previously seen in the literature for a simple Fe_3O_4 termination of hematite. Hematite samples which are pure simply disorder and reduce upon ion bombardment and no spinel phase can be detected. This is true independent of the type of impurity present. Regardless of the impurity concentration, samples which are annealed at 830–930 °C in a flow of oxygen for 2 h oxidize and (1×1) diffraction spots indicative of a bulk-truncated hematite surface are present.

It is important for those attempting surface science studies of hematite to be aware of the fact that in impure specimen (either mineralogical in origin or doped to enhance conductivity for scanning tunneling microscopy), this impurity-stabilized spinel phase can and does form under certain bombardment conditions and may be easily confused with a simple Fe_3O_4 termination (reconstruction) of hematite.

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