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Hydrated α-$Fe_2O_3(1\bar{1}02)$ surface structure: Role of surface preparation

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Abstract

The surface structure of α-$Fe_2O_3(1\bar{1}02)$ was studied under two different surface preparation conditions using crystal truncation rod (CTR) diffraction. Wet chemical and mechanical polishing (CMP) at 298 K results in a crystalline surface termination in which the top layer of iron atoms is absent compared to the stoichiometric bulk termination. Annealing in air at 773 K resulted in a transformation of the surface to a structure consistent with hydroxylation of the stoichiometric termination. These results agree with theoretical predictions of Lo et al. [C.S. Lo, K.S. Tanwar, A.M. Chaka, T.P. Trainor, Phys. Rev. B 75 (2007) 075425] and clearly show an ambient pressure surface preparation path leading to a stoichiometric hydroxylated surface, which is apparently a meta-stable configuration at room temperature.

Keywords: Iron oxide; Hematite $(1\bar{1}02)$; α-Fe_2O_3; Surface X-ray diffraction; Surface preparation; Surface annealing; Surface structure; Crystal truncation rods

Iron (hydr)oxides are abundant natural substrates that play an important role in the fate and transport of various contaminants, primarily through adsorption and surface precipitation processes [1,2]. Surface reactions involving these oxides also are critical in a variety of industrial applications including catalysis [3–6], metal oxide thin film preparation [7–10], corrosion research [11–14], data storage [15], and drug delivery [16]. The chemical properties (e.g. Lewis and Bronsted acid/base character) and overall reactivity of these oxides are dictated by the type and local structure of chemical moieties exposed at the interface [17], which are dependent on the chemical and physical history of the surface.

Numerous studies have focused on determining the surface structure of iron and aluminum oxides under ultra-high vacuum (UHV) conditions [18–23] as well as under hydrated conditions [24–27]. Not surprisingly, different structural terminations for the same surface are often observed, emphasizing the important role of surface preparation [26,27]. For example, the α-$Al_2O_3(0001)$ surface has three unique proposed surface structures resulting from three different surface preparations. A hydroxyl terminated α-$Al_2O_3(0001)$ surface was determined after a mild acid wash and air annealing at 623 K using crystal truncation rod (CTR) diffraction in a humidity cell [24], an Al terminated surface was identified via CTR after O_2 annealing in UHV at 1123 K [23], and a mixed Al/O terminated surface was observed with LEED after air annealing at 1773 K followed by O_2 annealing in UHV at 1173 K [20]. The α-$Al_2O_3(1\bar{1}02)$ surface also is known to have discrete surface structures depending on surface preparation, where a hydroxylated stoichiometric termination was determined after annealing in air at 623 K measured with CTR diffraction [26], while a sample annealed in air at 623 K followed by UHV O_2 annealing at 1273 K, and subsequently dosed with water (1×10^{-8} to 1.6 Torr) resulted in a termination

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with missing top layer of aluminum atoms measured with CTR diffraction in UHV [28].

The α-$Fe_2O_3(1\bar{1}02)$ surface has been previously studied using UHV techniques exhibiting either a (1×1) stoichiometric surface or a (2×1) reconstructed surface after annealing in O_2 [18,19,29]. Water adsorption was used to probe the surface reactivity of the (1×1) surface and resulted in a hydroxylated stoichiometric termination at temperatures <350 K [18,30]. We have previously studied the surface structure of the α-$Fe_2O_3(1\bar{1}02)$ prepared using a chemical mechanical polishing (CMP) procedure detailed elsewhere [27] under hydrated conditions at room temperature. The CMP prepared surface consistently results in a surface termination with a vacant top Fe layer compared to the ideal stoichiometric termination (Fig. 1) [27].

The observation of different chemical terminations for a given crystallographic orientation demonstrates the need to understand the relationship between surface preparation and the resultant surface structure. Because surface reactivity is strongly dependent on surface structure, any changes in the surface preparation may have substantial effects on the reactivity of the substrate. Currently, there are a limited number of non-UHV studies correlating specific surface terminations with surface preparation methods, hence there is a limited understanding about how to control surface structures through wet surface preparations. The present study provides a detailed experimental analysis of the role of ambient pressure preparation procedures on the structure of α-$Fe_2O_3(1\bar{1}02)$ surface.

Natural single crystals of α-$Fe_2O_3(1\bar{1}02)$ (~1 cm^2) obtained from Bahia, Brazil were prepared using a wet chemical mechanical polishing (CMP) procedure followed by mild acid etching (details are provided in Tanwar et al. [27]). The α-$Fe_2O_3(1\bar{1}02)$ sample was then annealed in air at 773 ± 2 K for 3 h in a pre-heated furnace. Following annealing the sample was allowed to equilibrate with room temperature (298 K) in a dessicator for 6 h. After cooling, the sample was mounted in an environmental cell used for surface diffraction measurements [31] and kept under water-saturated He atmosphere (relative humidity >90%, $pH_2O > 20$ Torr) to ensure that the surface remained fully hydrated [32].

Crystal truncation rod (CTR) experiments were performed on undulator beamline 13-ID at advanced photon source (APS) with a liquid N_2 cooled double crystal Si(1 1 1) monochromator and Rh-coated vertical and horizontal mirrors for focusing and harmonic rejection. All CTR experiments were conducted at 298 K using a 2 + 2 + kappa-geometry diffractometer with fixed incident energy of 12 keV. The surface diffraction intensities were collected in both specular and non-specular geometries by performing rocking scans through the CTR. The intensity of each rocking curve was background subtracted and corrected for active area, polarization, scan speed, and Lorentz factors to determine the individual structure factors [33]. The data set consisted of the four CTRs (Fig. 2) that are most sensitive to surface termination based on theoretical simulations of CTR profiles.

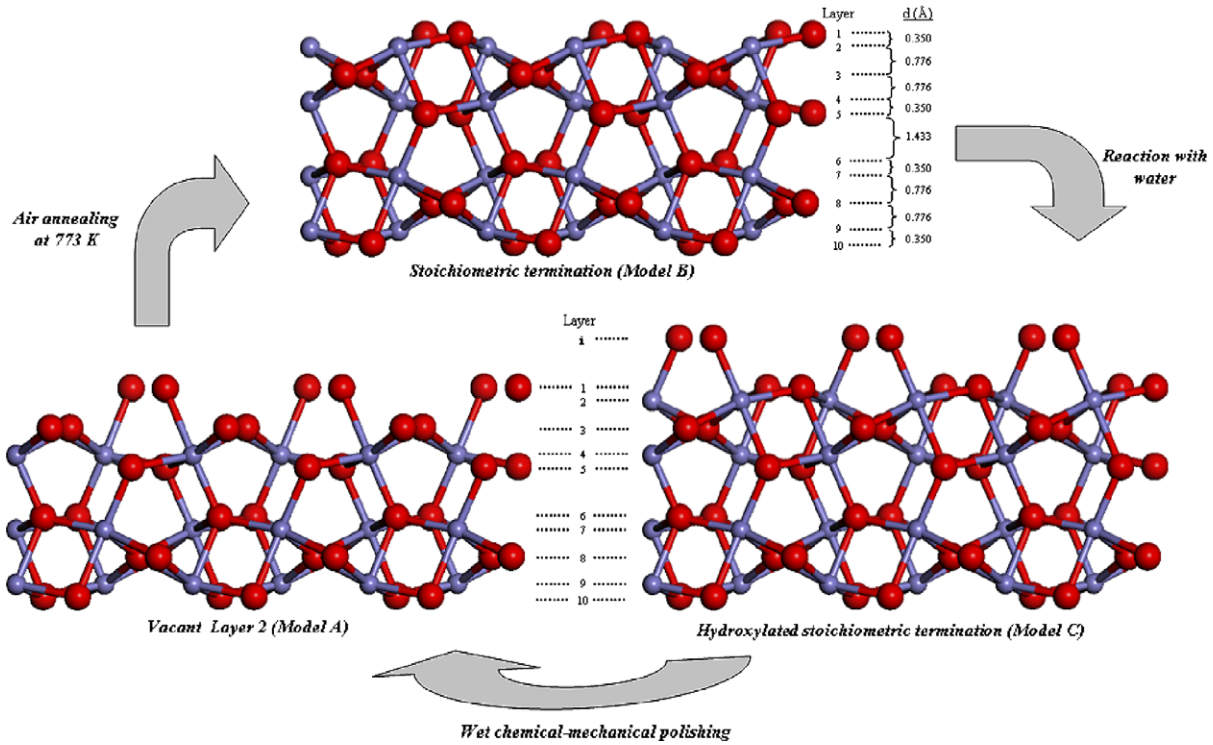

Fig. 1. Layer stacking sequence along the c_s axis for stoichiometric termination, the hydroxylated stoichiometric termination, and the termination with absent layer 2 iron. The large spheres are O atoms and small spheres are Fe atoms. Stacking sequences are shown with unrelaxed layer spacings.