

# X-ray standing wave study of vanadium oxide films on $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001)

C.-Y. Kim,<sup>1,2</sup> A. A. Escudro,<sup>1,2</sup> and M. J. Bedzyk<sup>1,2,3</sup>

<sup>1</sup>Department of Materials Science and Engineering, Northwestern University, Evanston, IL USA;

<sup>2</sup>Institute for Environmental Catalysis, Northwestern University, Evanston, IL USA;

<sup>3</sup>Materials Science Division, Argonne National Laboratory, Argonne, IL USA

## Introduction

Metallic or metal-oxide layers supported on different types of oxides have been extensively studied due to their wide applications in heterogeneous catalysis and gas sensors [1]. Despite this considerable interest, the morphology of the supported metal or metal oxide, the active sites, and role of supporting oxides in catalytic reaction need to be explored further to fully understand catalysis and to design new types of catalytic systems for specific reactions.

Supported vanadium oxide has been used in the manufacture of important chemicals and in the reduction of environmental pollution [2]. In supported vanadium oxide catalysis, the phenomenon known as monolayer catalysis has been reported [3], in which a submonolayer vanadium oxide film supported by an appropriate oxide displays greater catalytic activity when compared to multilayer vanadium oxide films. This monolayer enhanced catalysis demonstrates the significant role of the supporting oxide. The significance of the reducibility of the supporting oxide substrate has also been proposed [4].

As the most stable form of iron oxide, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has wide application in fields of heterogeneous catalysis, corrosion and gas sensing [1]. Vanadium oxide on hematite is an interesting system since V<sub>2</sub>O<sub>3</sub> vanadium oxide and hematite are isostructural, as both share the corundum structure. Vanadium oxides on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) has reported to grow as V<sub>2</sub>O<sub>3</sub> films [5]. In the present work, we report on x-ray standing wave (XSW) measurements of vanadium and vanadium oxide monolayer films grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001).

## Methods and Materials

The vanadium deposition and XSW measurements were conducted in an ultra-high vacuum (UHV) chamber (base pressure  $\sim 1.5 \times 10^{-10}$  Torr) located at the 5ID-C undulator DND-CAT experimental station at the Advanced Photon Source.

The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) sample was purchased from Commercial Crystal Laboratories as a 1.0 mm thick polished wafer. Degreased samples were mounted on a molybdenum sample holder, which could be heated from the backside by radiation from a hot tungsten filament. The sample temperature was monitored using an optical pyrometer and a thermocouple mounted near the sample holder. The clean surface was prepared by annealing the sample at 450 °C under a stream of atomic oxygen gas. The chamber pressure of  $1 \times 10^{-6}$  Torr was kept during sample annealing and also during cooling down to room temperature. The atomic oxygen flow was produced by passing molecular oxygen gas through a hot refractory capillary tube (Oxford Applied Research, TC50). Due to the directional flow of gas the actual oxygen partial pressure at the sample surface would be higher than the chamber pressure. Annealing in the atomic oxygen environment for 1 hour resulted in a sharp (1x1) LEED pattern.

A Knudsen cell evaporator was used to deposit 1.15 ML of vanadium (99.9%, Goodfellow) at a rate of 0.35 ML/min onto the room-temperature (RT) Fe<sub>2</sub>O<sub>3</sub>(0001) substrate. 1 ML of vanadium is defined as  $0.91 \times 10^{15}$  atoms/cm<sup>2</sup>, which is the

density of Fe atoms in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) surface. Ex-situ Rutherford backscattering spectroscopy (RBS) was used to measure the vanadium coverage after completion of the XSW experiment. After characterizing the as-deposited metallic vanadium film with XSW, vanadium oxides were then prepared by exposing the deposited vanadium to the atomic oxygen. The oxygen exposure was conducted at room temperature to avoid a possible inter-diffusion of vanadium to the hematite substrate.

The XSW measurements were conducted by scanning the sample in angle through the allowed Fe<sub>2</sub>O<sub>3</sub> (0006), (10  $\bar{1}$ 4), and (11  $\bar{2}$ 3) Bragg reflections and simultaneously collecting the diffracted beam intensity and x-ray fluorescence spectra at each angular step. The XSW measurements were collected using 7.0 keV x-rays that were conditioned by the high-heat-load 5ID Si(111) monochromator and a single Si(022) channel cut was used. In all cases, fitting the normalized reflectivity and V K $\alpha$  fluorescence yield with dynamical diffraction theory produced the coherent position ( $P_H$ ) and coherent fraction ( $f_H$ ) for the adsorbed V atoms.

## Results and Discussion

Experimental data and theoretical fits for the normal (0006) and the off-normal (10  $\bar{1}$ 4) and (11  $\bar{2}$ 3) XSW measurements are shown in Fig. 1 for the as-deposited V monolayer film on Fe<sub>2</sub>O<sub>3</sub>(0001). After oxidation with atomic oxygen, a (0006) XSW measurement was conducted, which resulted in the data and theoretical fit shown in Fig. 2. The change in the measured coherent position in the (0006) direction from  $P_{0006} = 0.60$  for the as-deposited vanadium film to  $P_{0006} = 0.88$  after oxidation corresponds to a change in height of the ordered V atoms of 0.64 Å. However, if we use the measured off-normal coherent positions of  $P_{11\bar{2}3} = 0.87$  and  $P_{10\bar{1}4} = 0.21$  to try to triangulate the position of the ordered V atoms, it becomes clear the measured coherent positions do not coincide with a unique adsorption site (although the intersection of the three measurements is close to a bulk-like O site). The idea that the vanadium atoms do not seem to occupy a unique adsorption site is understandable, given the high V coverage ( $> 1$  ML) and the possibility of multiple occupation sites. However, we have recently conducted further XSW experiments on this system, which involved lower V coverages and additional  $hkl$  Bragg reflections. Therefore, our recent XSW data can be used to generate a model-independent direct-space image of the V atomic density distribution, which will provide more insight into the V atomic arrangement.

While the full details of the V atomic distribution are not currently understood, the fact that there is a significant difference in the V adsorption geometry after oxidation remains important. This significant change can also be examined in light of our recent findings regarding the electronic structure of the V/Fe<sub>2</sub>O<sub>3</sub>(0001) system [6]. In this study, x-ray photoemission spectroscopy (XPS) results suggest the initial growth of vanadium films involves the transfer of electrons from V to the underlying substrate, causing a reduction of the Fe ions. Above a coverage of 2/3 ML, metallic vanadium is grown. The exposure

of vanadium film to atomic oxygen in the same process used in the present XSW study caused the conversion of the vanadium film to a  $V_2O_5$  film, as well as the re-oxidation of the  $\alpha$ - $Fe_2O_3(0001)$  at the film-substrate interface. Our current XSW result points to this reduction and re-oxidation process is accompanied by a significant rearrangement of the V atoms.

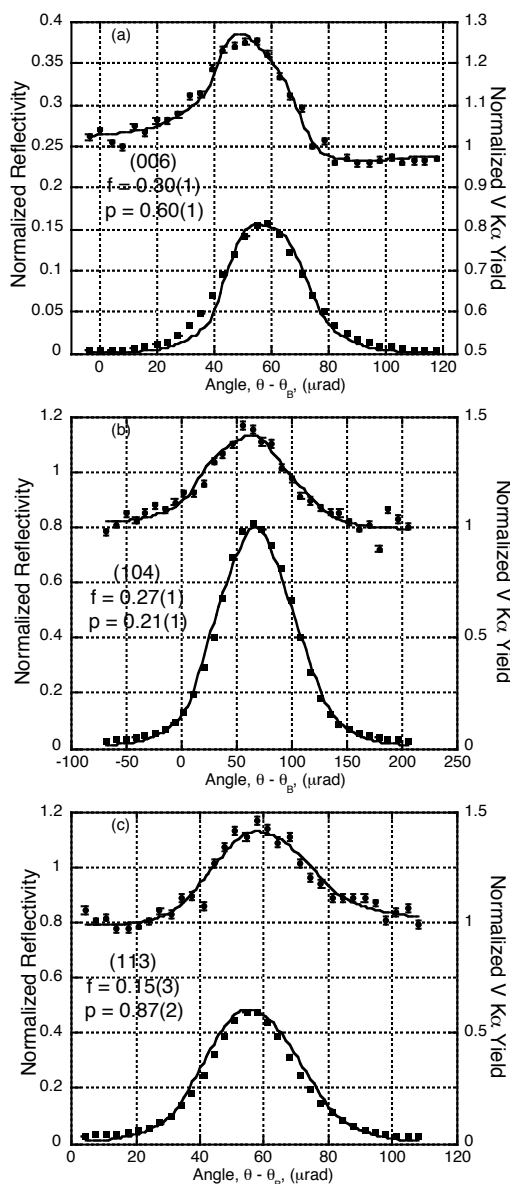


Fig. 1. Reflectivity and normalized V  $K\alpha$  fluorescence yields experimental data along with corresponding theoretical fits for the (a)  $Fe_2O_3(0006)$ , (b)  $Fe_2O_3(10\bar{1}4)$ , and (c)  $Fe_2O_3(11\bar{2}3)$  XSW measurements of the as-deposited vanadium film.

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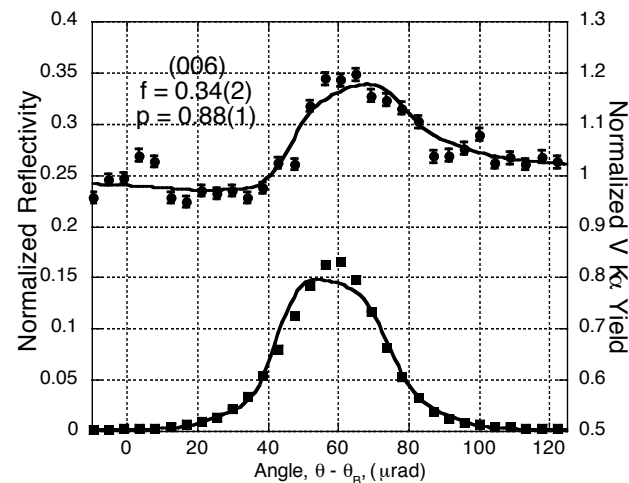


Fig. 2. Reflectivity and normalized V  $K\alpha$  fluorescence yield experimental data along with corresponding theoretical fits for the  $Fe_2O_3(0006)$  XSW measurements of the vanadium oxide film after atomic oxygen exposure.